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CHARACTERIZATION OF SULFUR RECOVERY IN OIL AND NATURAL GAS PRODUCTION

Keshava S. Murthy

Battelle Columbus Laboratories

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August 1974

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CHARACTERIZATION OF SULFUR RECOVERY IN OIL AND NATURAL GAS PRODUCTION

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Information is presented on production processes at natural gas fields, the resulting sulfurous emissions and how they are controlled. References are included.

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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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Task 6

EPA Project Officer: William Herring

Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
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ABSTRACT

The U. S. oil and natural gas production and processing systems are described. The sources of sulfur emissions in these systems as well as the current methods of control of such emissions are traced. Fourteen major and four minor processes for sweetening (removing H_2S) sour gas, two processes (Claus and Stretford) for production of sulfur and six processes for tail gas cleanup are described. Some factors that may help choose a process for a particular application are also indicated. The location of 84 Claus sulfur production plants used in natural gas facilities, their design capacity, and production data are tabulated. The contribution of SO_2 emissions from the natural gas processing industry to the national SO_2 emission is compared and described. Control options available for different levels of hypothetical allowable sulfur emissions from the natural gas industry are described. This report was prepared for the Office of Air Quality Planning and Standards of the U. S. Environmental Protection Agency, Contract No. 68-02-0611, and submitted on July 29, 1974.

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CONCLUSIONS

1. The U.S. oil and natural gas industry operated 795 gas processing plants of various capacities with a total processed gas volume of 1.6 billion scumd (56 billion scfd) as of January, 1973[a].
2. About two percent of the processed gas volume was handled in small plants with production less than 0.3 million scumd (10 MM scfd). However, the small plants numbered 206 (or 26 number percent).
3. About 83 percent of the total processed gas volume was handled in plants larger than 1.13 scumd (40 MM scfd) in production volume.
4. Reported gas volume associated with sulfur production data[1]* indicate that only about two percent of all natural gas processed was sour (i.e., contaminated with H_2S[b] and other sulfur bearing compounds like COS, CS_2, and RSH). However, if plants that do process sour gas but do not report sulfur production due to flaring of the acid gas[b] are included, estimated sour gas volume may be about five percent of total gas production.
5. The most widely used processes for removal of H_2S and other sulfur compounds from sour natural gas are the MEA, Sulfinol, DGA, Selexol and Benfield. Most widely used process for production of sulfur from acid gases is the Claus process.
6. During 1973, there were 84 Claus plants (detailed in Table 11) in natural gas processing with design capacities ranging from 1 to 1250 MT/D of sulfur output. The total design capacity was 6249 MT/D while the reported actual production was 2443 MT/D as detailed in Table 15. The number of plants with different capacities were as follows: 2 plants with up to 2 MT/D; 14 plants with 2 to 10 MT/D; 34 plants with 41 to 600 MT/D; and one plant with 1250 MT/D. Estimated range of efficiencies of the plants is 90 to 97 percent.

(a) Conversion factors are provided in Appendix G.
* References are listed on Page 71.
(b) See footnote on Page 1 for explanation.

7. If the maximum allowable emission limit (MAL) of sulfur per sulfur recovery unit (SRU) is limited at 1.0 MT/D, the 84 plants would emit 61,320 MT/Y of sulfur dioxide. This quantity of SO_2 represents 0.18 percent of the national SO_2 emissions based on 1972 data. To achieve the 1.0 MT/D sulfur emission limit, at least 34 Claus units or SRUs will be required to have conversion efficiencies in the range of 97.56 to 99.7 percent as described in Table 19.

8. If the MAL is raised to 2.0 MT/D of sulfur, the total SO_2 emission will be 122,640 MT/Y which represents about 0.36 percent of the national SO_2 emission of 33 million MT/Y for 1972. Thus, required efficiency of SRUs will be in the range of 95 to 99.6 percent for at least 34 units as detailed in Table 20.

9. Achieving the required SRU efficiencies to meet the MAL of 2.0 MT/D of sulfur is believed to require a significantly lower expenditure of electrical energy (which, therefore, is related to the national goal of energy resource conservation where possible) than the achievement of MAL of one MT/D of sulfur. Capital and other operating costs of achieving the former may also be significantly lower. The tradeoffs in environmental burdens to be considered as a consequence of decreased SO_2 emissions from SRU are as follows:

    (a) Increased SO_2 emission at power generating plants from increased electrical energy requirements

    (b) Increased fine particle emissions at power plants that escape the most advanced particulate collectors like high efficiency electrostatic precipitators

    (c) Any increase in water pollution and solid waste burden caused by SRU tail gas units

10. Tail gas cleaning systems are available to increase sulfur recovery of Claus plants to 99.7 percent or higher. Some experimental data are reported which support the view that new Claus plants can be designed and operated to obtain 99.3 percent efficiency.

RECOMMENDATIONS

On the basis of this study, it is recommended that:

1. Consideration should be given to estimating any energy savings that may be realized by adopting a hypothetical allowable sulfur emission of 2.0 MT/D or 3.0 MT/D (see Tables 19 and 20) as compared to 1.0 MT/D or any other allowable sulfur emission level.
2. Due consideration should be given to setting emission levels that would help to continue the existence and growth of energy supply from the small gas processing plants.
3. Specific control equipment or control option should not be specified so that the optimum combination of options suitable for each processing facility can be chosen for each control category and allowable emission limit.
4. The cost of various options for the different control categories be studied to help in understanding the control cost-benefit relationship.
5. Evaluation should be made of the possibility of realizing improved Claus plant efficiency of 98 percent and higher by exploring this aspect in depth and by considering the possibility of providing the needed lead time for the industry to evaluate this very desirable alternative.

CHARACTERIZATION OF SULFUR RECOVERY IN OIL AND NATURAL GAS PRODUCTION
(Contract No. 68-02-0611, Task 6)

by

Keshava S. Murthy

INTRODUCTION

Production of petroleum (crude oil) is almost always associated with production of substantial quantities of natural gas. Production wells are classified as gas wells when the ratio of gas to oil produced is high. When the oil-to-gas ratio is high, however, the production facility is considered an oil well. An arbitrary definition of a gas well is that it can product up to 31.8 kltr (200 bbl)[a] of oil per 28,000 cu m (10^6 cu ft) of gas. A higher oil-to-gas ratio in the production well could place it in the oil well category. These classifications are aribitrary and are merely a convenience.

The natural gas processing plant with the lowest gas production reported[1] for 1973 had an output of 8400 cu m/day (0.3 x 10^6 cu ft per day) in Texas (Ranchland Plant, Midland County); the highest plant throughput was 52.7 x 10^6 cu m/day (1971 x 10^6 cu ft/day) also in Texas.

About five percent of the U. S. natural gas production is sour.[b] Consequently, treating to remove the acid gas[b] constituents is required.

(a) Metric System is used in this report and conversion factors are provided in Appendix G.

(b) Sour gas in industry jargon implies gas contaminated with sulfur in excess of pipeline specifications mainly in the form of hydrogen sulfide (H_2S) and carbon dioxide (CO_2), both of which are also called the "acid gas" constituents of natural gas. Many gas streams, however, particularly those in a refinery and manufactured gases may contain mercaptains (RSH), carbon disulfide (CS_2) and/or carbonyl sulfide (COS). The latter three are often products of refinery processing and usually only appear in small concentrations in natural gas streams.

The treatment process is usually designed for the product natural gas to conform to the general pipeline specification of one quarter grain or one grain of H_2S per 100 standard cubic feet of gas. The "quarter grain gas" is equivalent to 4 parts per million by volume (ppmv) of H_2S.*

Pipeline gas specifications are known to range from 6 to 23 mg/s cu m (0.25 to 1.0 grain/100 scf). Pipeline companies' specifications for other sulfur compounds in natural gas are not common. However, the total sulfur content of the gas is specified usually at 120 to 480 mg/s cu m (5 to 20 grains per 100 scf).

Processes used for sweetening the sour gas are generally either amine treatment processes or modifications thereof. These are discussed in this report. Other processes used are the hot carbonate process, the fluor solvent process, etc. Depending upon the ratio of CO_2 and H_2S in the feed gas, the acid gas from these processes may be rich in H_2S. The methods of removal of the H_2S and CO_2 from the natural gas and subsequent handling or disposal of the H_2S in an environmentally sound manner form the subject of this report.

Objective

The overall objective of this study (Task 6 under Contract No. 68-02-0611) is to assist the Office of Air Quality Planning and Standards, Environmental Protection Agency in developing standards of performance for sulfur removal and recovery associated with the production of oil and natural gas. The study is concerned with the identification of: (1) sources of sulfur emissions, (2) current methods of sulfur recovery, (3) potential improved methods of sulfur recovery, and (4) efficiencies of sulfur recovery, for gas processing facilities of small, intermediate, and large sizes. From this information, recommendations for performance standards for the three facility sizes are to be developed. Specific subtasks to be completed to achieve the overall objective are as follows.

---

* For a gas of 0.65 specific gravity the 4 ppm of H_2S is equivalent to approximately 7 parts per million by weight (ppmw). In the metric system a quarter grain gas contains approximately 6 mg of H_2S per standard cu m of gas.

(1) Describe the oil and gas processing and production systems using typical example facilities. Provide quantity and composition of sulfur constituents in the systems described.

(2) Describe lesser known or novel sulfur removal processes used in oil and gas fields with reasons for their choice. Provide quantity and composition of sulfur constituents in the systems or processes described.

(3) Provide comparative description of natural gas and refinery gas compositions and define similarities and differences in processing methods.

(4) Compare methods of sulfur production from acid gases and tail gas conditioning processes.

(5) Provide statistical summary of sulfur recovery plants used in production and processing of oil and natural gas.

(6) Relate sulfur emissions from natural gas processing systems to overall national sulfur emissions.

(7) Provide operational details of selected oil and gas sweetening processes.

(8) Provide an overall assessment of the problems with suitable conclusions and recommendations.

Methodology

Understanding the industry as thoroughly as possible can be considered a prerequisite to the characterization of the problems and methods of sulfur recovery in oil and gas processing areas. Therefore considerable effort was expended in the direction of familiarization with the processing techniques by (a) field visits to processing units, (b) discussions with process engineers and plant superintendent of several production companies, (c) study of latest publications on

the gas processing techniques, (d) contact with academicia, and (e) contact with manufacturers of equipment for sulfur removal and recovery. To obtain insight into the Control philosophy of the state control agencies, discussions were held with the state agencies in Texas, Louisiana, and Oklahoma via telephone and visits as appropriate.

The visits and discussions described above and listed in Appendix E were useful. The data and surveys reported in the Oil and Gas Journal[1] were a good starting point for approaching the industry base and classifying the industry into size groups. The Oil and Gas Journal Survey data for the states of Louisiana and Texas were verified for completeness and accuracy by direct contact with gas process engineers of several energy companies.

The steps used in conducting this study to achieve the goals of identifying control options can be summarized as follows:

(1) Survey open literature

(2) Visit processing facilities, meet industry personnel, and identify additional sources of useful and critical data

(3) Visit and/or discuss with state air-pollution control agencies their experience in the control of sulfurous emissions and related problems from oil and natural gas processing

(4) Analyze the problem in light of the above discussions, plant visits, and open literature survey

(5) Apply the results of analyses to preparation of draft final report

(6) Obtain review of the draft document from EPA

(7) Prepare final report.

I. OIL AND NATURAL-GAS PRODUCTION AND PROCESSING SYSTEMS

Petroleum is a complex mixture of low- and high-volatile organic compounds. Most of the less-volatile compounds (pentane and higher carbon compounds) can be considered to comprise the oil portion while the more-volatile compounds such as methane, ethane, and some propane are predominantly in the natural-gas portion of petroleum. Butanes which have boiling points ranging from -11.7 to -0.56 C (11 to 31 F) occur in both the gas and oil fractions in substantial amounts.

Because the oil and gas occur together in the reservoir, field facilities for oil and gas processing usually handle both oil and gas. Usually the field processing of the oil is limited to its physical separation from the gas; the separated oil is not generally subject to further processing in the field but is delivered to refineries for processing into various products. Therefore, this report is concerned primarily with the processing of natural gas only.

Depending on the well output, producing and natural-gas processing facilities can be classified into small, intermediate, and large sizes. An arbitrary size classification is presented below:

Size Range	Gas Production	
	Million scf/day	Million cu m/day
Small	0.5 to 9	Up to 0.3
Intermediate	9.1 to 40	0.3 to 1.13
Large	40.1 to 1971*	1.13 to 51.0

Natural gas dissolved in the crude oil underground acts as a buoyant medium for conveying the oil to the surface in the "Dissolved-Gas-Drive" method of production. Usually the oil production ranges from six to several hundred kiloliters per MMscum (10 to several hundred barrels per million cubic foot) of gas produced.

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* Largest reported facility.

Most oil and gas wells produce at the highest rates during the initial period of production. Since the production rate usually decreases with the age of the well, a large processing facility would normally have then become intermediate-sized, then small-sized, and finally shut down. However, there are numerous small gas and oil wells that are operated on a part-time basis by ranch hands.

Types of Processing Facilities

The facility type is a function of production capacity and the constituents present in the oil and gas. For example, if the gas volume is in the intermediate range and the gas has significant amounts of propanes and butanes (NCL components), the facility would be more complex than a simple gas-treating facility. Similarly, if the gas is sweet (free of H_2S as >90 percent of all gas wells are) and does not contain recoverable amounts of heavier hydrocarbons, the facility will be very simple in that the gas after water removal is sold directly to pipeline companies.

An example of a complex facility is the Bryans Mill Gas Processing Plant at Bryans Mill, Texas, operated by Shell Oil Company. This plant produces about 1.42 million s cu m/day (50 MM scf/day) of gas associated with about 1590 kltr (100,000 bbl) of oil per day. The Claus unit produces 203 MT/day of sulfur (200 LT/day). The gas from this plant is recompressed to about 253 Kg/cm^2 (3600 psi) of pressure and reinjected to maintain sufficient reservoir pressure. One of the purposes of the facility is to produce sulfur which has a ready market in this area. This facility is not typical in that almost all of the gas produced is recompressed and reinjected into the reservoir. The facility operates as a secondary oil-recovery operation and uses refrigerated absorption to produce 188 kiloliters (47,000 gallons) of liquid propane and 235 kl (62,000 gallons) of combined gasoline/LP gas per day.

Other facilities produce gas for sales, LPG (propane and butanes), natural-gas liquids, and crude oil.

Size Range of Gas Processing Facilities

The Oil and Gas Journal Annual Survey for 1973 indicated that during 1972, a total of 795 gas processing facilities in the U.S. produced 1.606 billion cu m (56.7 billion cubic feet) per day of natural gas, and 295610 kltr (78.1 million gallons) per day of natural gas liquids. The sulfur production per day was ~ 2480 MT/D (2445 long tons/day).

The 795 gas-processing facilities were fed by about 120,000 individual gas/oil wells, each facility processing on the average the output from about 10 wells. The size of the 795 facilities ranged from 8400 cu m (0.3 million cft) to 52.7 million cu m (1971 million cft) per day. Table 1 provides detailed size classification of the processing plants by state for the 24 states in which gas-processing facilities are reported to exist. Although the survey reports that industry response to the questionnarie by the Oil and Gas Journal was substantially 100%, it is quite possible that some small gas processors who flare or emit H_2S as-is from their amine treatment units may not have responded. By and large, the data in Table 1 provide a relatively complete picture of the industry. A summary of the data is tabulated below.

Size Range	Number of Plants		Total Production	
MMscfd	Number	Percent	MMscfd	Percent
0.5 to 9.0	206	26%	1046.6	1.9
9.1 to 40	319	40%	8798.4	15.4
40.1 to 1800	270	34%	46942	82.7
Total	795	100	56787	100

The data show significantly that although the plants in the small size range amount to 26 number percent of the facilities, only 1.9 of the total U.S. gas plant capacity is in this size range. It is also significant that as of January, 1973, 82.7 percent of gas production and processing was done in the large size range plants.

TABLE 1. CLASSIFICATION OF U.S. GAS PROCESSING FACILITIES BY STATE AND SIZE (JANUARY, 1973)

State	Number of Gas Plants	Gas Production Per Day		0.5 to 9.0 MMscfd			9.1 to 40 MMscfd			40.1 to 800 MMscfd		
		MMscumd**	MMscfd	Number of Plants	MMscumd	Total Production MMscfd	Number of Plants	MMscumd	Total Production MMscfd	Number of Plants	MMscumd	Total Production MMscfd
Alabama	1	0.034	1.2	1	0.034	1.2	-					
Alaska	2	0.92	32.5	1	0.14	4.9	1	0.78	27.6			
Arizona	1	0.057	2.0	1	0.057	2.0						
Arkansas	3	2.41	85	1	0.76	2.7	2	2.33	82.3			
California	49	24.92	880	21	4.02	142	23	11.55	408	5	9.35	330
Colorado	12	10.11	357	6	1.02	36	5	1.87	66	1	7.22	255
Florida	10	22.09	780				9*	3.68	130	1	18.41	650
Illinois	1	14.73	520							1	14.73	520
Kansas	29	136.47	4,819	5	0.79	28	9	5.41	191	15	130.27	4,600
Kentucky	2	22.37	790							2	22.37	790
Louisiana	132	553.57	19,547	20	2.29	81	37	18.21	640	75	533.15	18,826
Michigan	5	3.12	110	1	0.028	1.0	3	1.78	63	1	1.30	46
Mississippi	10	2.61	92	7	1.076	38	3	1.53	54			
Montana	4	0.85	30	3	0.283	10	1	0.57	20			
Nebraska	2	0.34	12	2	0.34	12						
New Mexico	36	88.78	3,135	4	0.51	18	10	3.40	120	22	84.88	2,997
North Dakota	3	2.80	99	1	0.24	8.5	1	0.44	15.5	1	2.12	75
Oklahoma	86	95.52	3,373	23	5.66	200	35	30.02	1,060	28	59.84	2,113
Pennsylvania	2	0.093	3.3	2	0.093	3.3						
S. Dakota	1	0.71	25				1	0.71	25			
Texas	369	590.56	20,853	93	11.33	400	167	160.74	5,676	109	418.48	14,777
Utah	4	3.43	121	1	0.17	6	2	1.02	36	1	2.24	79
W. Virginia	4	7.56	267				2	0.99	35	2	6.57	232
Wyoming	27	24.16	853	13	1.47	52	8	4.22	149	6	18.46	652
Total	795	1608.21	56,787	206	29.64	1,046.6	319	249.17	8,798.4	270	1329.4	46,942

* 13% H_2S.

** MMscumd = million standard cubic meters per day.

Detailed Description of Small, Intermediate and Large Size Facilities

Distinctions between small and large facilities are not very useful because the unit processes used in a particular facility do not depend on the plant size but on the gas composition. Accordingly, if the gas is sour (>23 milligrams per s cu m) and rich (or wet i.e. containing >1.34 liters of liquids per s cu m of gas), even the smallest facility will be forced to use a gas sweetening process and a liquid recovery unit. On the other hand if large quantities of sweet gases are produced, as 90% of the gas wells do, even large plants processing more than one billion cubic feet daily do not use sweetening units.

However, one important difference between small and large plants processing sour gas is in the area of sulfur recovery from acid gases. Usually, if the volume of acid gas generated is insufficient to produce enough sulfur (~2 MT per day), small plants flare the acid gas instead of recovering the sulfur. The large plants usually practice sulfur recovery because of the large volume of acid gas they generate and the consequent sulfur value contained in the acid gas.

Description of Small and Intermediate Processing Facilities

A schematic block diagram of typical gas-processing facilities in this size range is presented in Figure 1. The facility represented here can handle both sweet and sour gas. A very small facility would only employ processes (1), (3), (4), (6), and (8) identified in the figure. The description of the process steps and associated environmental burdens follow.

Stage Separation (1).* Gas from the wells enters the stage separators where the oil is separated from the gas and the pressure of the gas is reduced from about 150 atm to pipeline requirements, usually about 70 atm.

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* Number refers to block number in Figure 1.

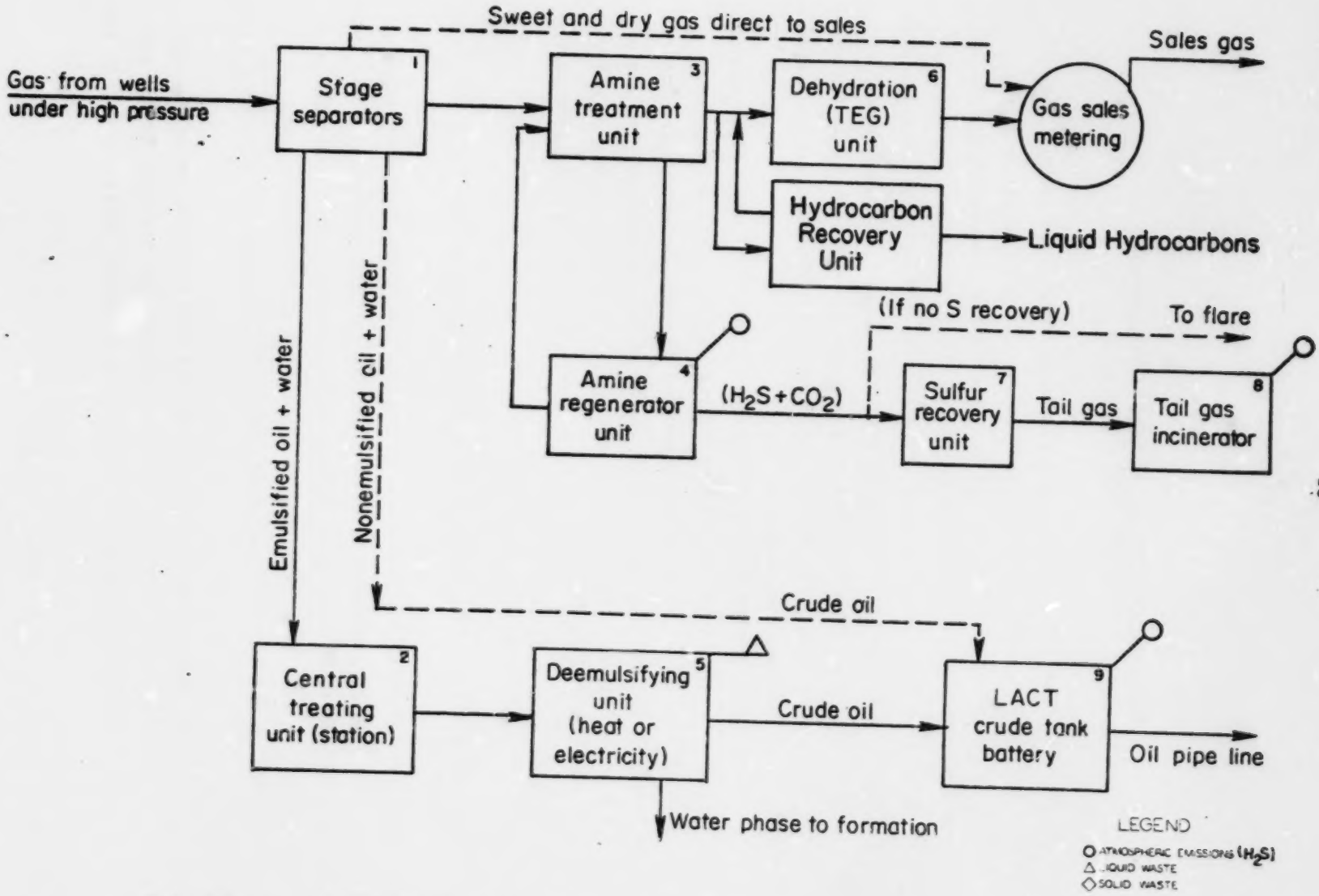

FIGURE 1. SCHEMATIC OF A SMALL (OR INTERMEDIATE) GAS PROCESSING FACILITY

The oil is then flashed in several stages to insure maximum oil recovery and the flash vapors are recompressed to pipeline pressure.

Products from this process step are, (1) sour or sweet gas and (2) crude oil. If the gas is sweet and dry (free of water), it is sold to pipe line companies via the sales metering station (8). If the gas is sour, it is routed to step (3) which is described later. Similarly, the crude petroleum oil is sent to step (2) or step (9) as shown in Figure 1. This process produces no environmental burdens.

Central Treating Unit (2). When the crude oil from step (1) is an emulsified mixture of oil and water it is pumped to a central treating facility. De-emulsifying treatment followed here is described in step (5).

Amine Treatment (3). Amine treatment removes the undesirable H_2S (and CO_2) from the sour gas produced in step (1) stage separators. The more common amine treatment processes currently in use are: the monoethanol amine (MEA) process, the Shell sulfinol process, the Diethanol amine (DEA) process, and the Econamine process. Details of these processes are discussed elsewhere in this report. These processes are usually carried out at high pressures. The process produces "quarter-grain" to one-grain gas which is equivalent to about 4 to 16 ppm H_2S by volume.

There are no environmental burdens from this process step.

Amine Regenerator (4). The spent amine solution in step (3) is continuously regenerated in an amine regenerator. Usually the process involves warming of the solution plus stripping to desorb the H_2S and CO_2.

The process produces H_2S and CO_2 which are the major components of the "acid gas". Generally the acid gas is fed to a sulfur recovery plant.

The major environmental burden from the regenerator is H_2S. If the acid gas is not processed to recover sulfur, it is flared, which results in emission of sulfur dioxide to the atmosphere.

De-emulsifying Process (5). Treatment of the oil-water emulsion is necessary whenever the stage separation process step (1) generates an emulsified crude oil-water mixture. The most common methods of emulsion

treating use chemicals or heat, or both. The kind of treating method is determined by the characteristics of the emulsion. The treatment is normally done with a "heater", or "heater-treater". The heat is supplied by means of a burner which uses either gas or fuel oil; and if chemicals are used, they are injected in small quantities by pumps like those used for corrosion treating. A great variety of chemicals are used for this purpose, but no one material has proved effective for all emulsions.

After being heated and/or chemically treated, the emulsion is allowed to enter a tank where the water can separate from the oil. The separated liquids are then drawn off-the oil going to the stock tanks, and the water going to the disposal system. Recently the use of electrical currents to break emulsions is gaining acceptance.

Major environmental burden is salt water separated in the process. The water is returned to well formations; when this is not feasible, water treatment is employed so that the discharged water is accepted without endangering the safety of the waterways.

Dehydration (6). Sweet gas from the amine treatment units is contaminated with water vapor. Removal of this water vapor is usually done by using triethylene glycol (TEG), an alcohol which can absorb only the water very effectively.

Product from this process is dry natural gas ready for sale. There are no environmental burdens from this process.

Sulfur Recovery (7). Acid gas from the amine regenerator step (4) is often rich in H_2S and by suitable processing, is converted to pure elemental sulfur* in this process. The most common sulfur-recovery process employed is the modified Claus Process which has a recovery efficiency limit of 90-97 percent.

Product from this process is pure sulfur.

The major environmental burden of this process is a tail gas from the plant which contains about 3 to 4 percent H_2S in the feed.

Tail-Gas Incineration (8). Unconverted H_2S, sulfur vapors, and other sulfur compounds from the Claus sulfur plant are burned to sulfur

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* Sulfur purity exceeds 99.5 percent.

dioxide (SO_2) in this unit. Fuel for combustion is provided by plant fuel gas or by flash vapors and vapor from sour water strippers (if there are any).

This step is the major contributor to environmental burden. The emission of SO_2 to ambient air is the major problem of Claus plants. This is discussed in detail in other sections of this report.

LACT* Crude Tank Battery (9). This system provides for the unattended transfer of the oil (or gas) from the lease to the pipelines. The oil storage tanks in this system are under a positive pressure. When no vapor recovery system is installed, a small amount of hydrocarbon vapor contaminated with H_2S (if the oil is sour) is lost to ambient air.

Environmental burden from this unit consists of loss of H_2S and Hydrocarbons as vapors from oil tanks. The emissions are not significant however. Most of the new tanks are equipped with vapor recovery units, thus reducing the emissions to near zero.

Description of Large Natural Gas Processing Facilities

The essential differences between large processing installations and the smaller facilities are as follows.

(1) The large facilities can often justify a sulfur-recovery plant with recovery efficiencies of up to 97 percent. This implies that three recovery stages will be used in the Claus plant.

(2) Large units are more likely to have hydrocarbon recovery plants that produce liquid propane, liquid butanes, and gasoline-blending cuts.

A schematic of a typical large facility is presented in Figure 2. This plant produces crude oil with a Reid Vapor Pressure (RVP) of 8 psi (about 0.5 atm), sales gas, propane, butanes, natural gasoline, and elemental sulfur.

Figure 3 provides a detailed flow scheme of just the sulfur-recovery plant shown in Figure 2.

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*Lease Automatic Custory Transfer.

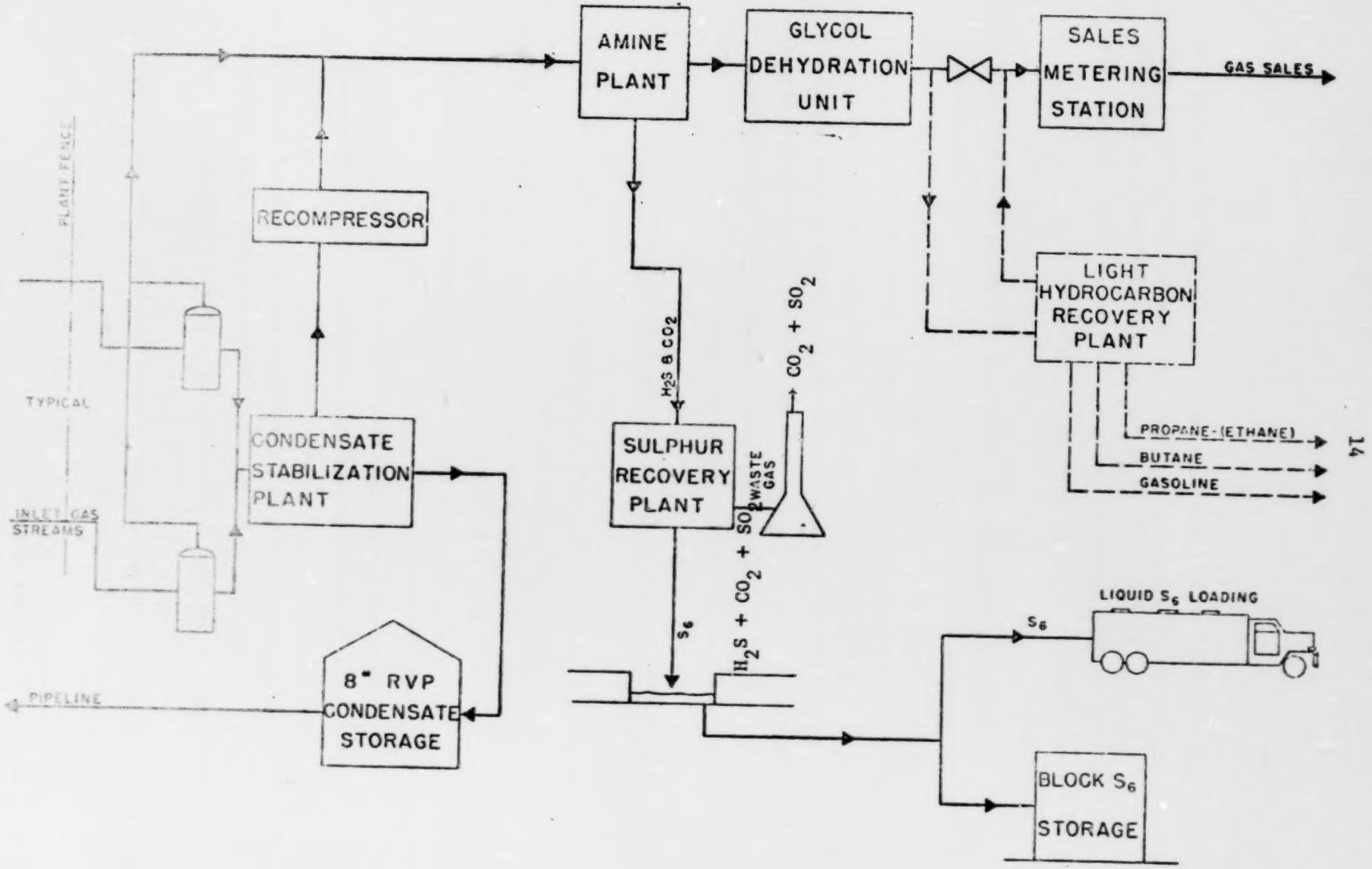

FIGURE 2. TYPICAL LARGE NATURAL GAS PROCESSING FACILITY

Both Figures 2 and 3 are self-explanatory. However, the sources of H_2S and SO_2 emissions need discussion.

Sources of Sulfur Emissions

The sources are: (1) the tail gas from the Claus plant final sulfur separator, (2) the salt-water flash tank, and (3) the salt-water stripper.

Tail Gas from Claus Plant. The quantity of H_2S present in the tail gas depends on the following factors: (1) the H_2S in Claus plant feed, (2) the conversion efficiency of the plant which is a function of the number of stages of sulfur reactors, (3) degree of precision in the control of the temperature in the Claus plant burners, and (4) the instrumentation employed in controlling the plant-operating conditions.

Rankine, et al[2] predict that theoretical thermodynamic recoveries from a four-stage Claus plant, processing a feed containing 67 percent hydrogen sulfide, to be as follows:

2 catalytic stage recovery 97.9 percent
3 catalytic stage recovery 99.1 percent
4 catalytic stage recovery 99.4 percent.

However, actual yields of sulfur in existing plants has been about 90 to 97 percent. This leaves about 3 to 10 percent of the feed H_2S in the tail gas.

Salt-Water Flash Tank. A considerable quantity of salt water (also called sour water if dissolved H_2S is present) is produced from oil-water separators. One plant reports a salt-water production of one percent by volume of the oil production (one liter/100 liters of oil) and on the basis of gas production, 4.63 kiloliters of salt water/million cu m of gas produced. These statistics are not typical because salt-water production ranges from 1 to as much as 99 percent of total well output. Reported H_2S content of sour waters also varies, a typical value being 0.5 gram/liter of sour water.

Disposal of the sour water requires that the H_2S in it be stripped. This is accomplished in flash tanks and strippers. Because the sour-water

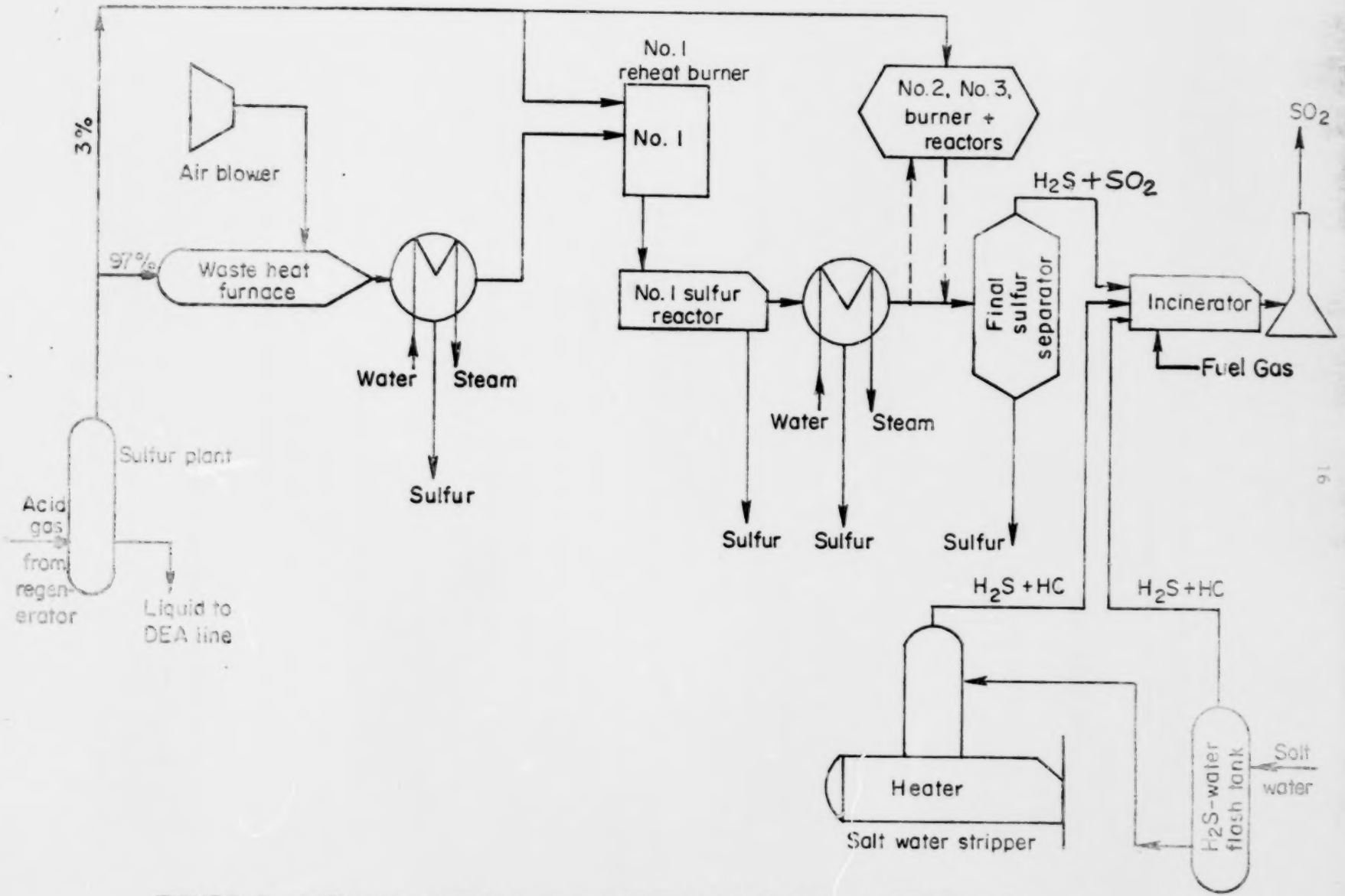

FIGURE 3. DETAILED SCHEMATIC OF SULFUR RECOVERY (CLAUS) PLANT

stripper gas contains some amounts of hydrocarbons (HC), the gases are often fed to the Claus tail-gas incinerator. It is not known if this practice is followed by all processing plants.

It is possible to compress the gas from the stripper or operate the sour-water stripper at about 0.5 atmospheres (~7.5 psig) so that the gases can be fed to the Claus plant. However, if the hydrocarbon content of the gas is high, removal of heavy hydrocarbons will be necessary to insure that the purity and color of the Claus plant sulfur is maintained.

Emission Sources of Other Sulfur Compounds. The natural gas industry is predominantly concerned with H_2S as an undesirable constituent in natural gas. However, other organic sulfur compounds that can be present in both raw and processed natural gas are: mercaptans (RSH), carbonyl sulfide (COS) and carbon disulfide (CS_2). Some of the sweetening processes are more effective in removal of these other sulfur compounds. There is also evidence[3] that undesirable side reactions in a Claus plant tend to form COS and CS_2. It is estimated that as much as 2 percent of the sulfur in the feed might be converted to organic sulfur compounds, and that this might account for 40 percent of the SO_2 in the incinerated gases[4].

In summary, although COS and CS_2 can be formed in a Claus plant, their exact source (point location) is difficult to identify. However, these compounds end up in the tail gas. Also the raw gas can contain significant amounts of COS, and RSH as shown in Table 7. The CS_2 content of natural sour gases is very low. By a judicious selection of the sweetening process, up to 90 percent of these compounds can be taken out of the natural gas. However the acid gas will concentrate the organic sulfur compounds and when fed to the Claus plant, these compounds constitute emissions in the tail gas. Recently, catalysts (example Cobalt-Molybdynum) to hydrolyze COS and CS_2 to H_2S and CO_2 have been identified[4]. It appears possible that improved catalysts can reduce unconverted CS_2 and COS concentrations in the tail gas and hence the SO_2 emission in the incineration of gases.

II. COMPOSITION OF NATURAL GAS AND REFINERY FUEL GASES

The U.S. Bureau of Mines reports[5] that as of December 31, 1972, there were 121,153 producing wells for gas and condensates in the United States. These wells were distributed over 30 states. Generally, the composition of gas from these wells varies from well to well. However for processing purposes they must be grouped. Thus, sour and sweet is one type of grouping, and, rich (or wet) and dry gas is another type of grouping. Both groupings are necessary and significant. Sour gas contains considerably more than 2.29 grams/100 s cu m (1 grain of H_2S per 100 scf) and must be sweetened by amine or other processing methods described in Appendix A. Rich gas is gas containing more than 1.34 litres of liquid components (propane and higher-boiling compounds) per s cu m of gas (10 gallons/1000 s cu ft). Dry gas usually contains less than 0.5 gallons of propane plus compounds per 1000 cft and hence, recovery of natural-gas liquids (NGL) from dry gas is usually not economically warranted. Natural gas exists at high pressures (20 atm and above) which helps in amine treatment. Also, because most natural gases are free of very heavy hydrocarbons, aromatics, and olefins, the treatment of acid gas to produce bright yellow sulfur in a Claus unit is much easier. Composition of various samples of natural gases are presented in Tables 2 and 3. Detailed analyses of sulfur compounds in natural gas are presented in Table 4.

Composition of Refinery Fuel Gas

Refinery fuel gases originate in the refinery from many cracking and catalytic processes. Examples of gas producing processing are: thermal cracking, catalytic cracking, sour water stripping, topping, hydrotreating, etc. Gases from these processes usually are contaminated with H_2S. Typical analyses of refinery fuel gases are not available because most refineries do not record the analyses of the fuel gases except for their H_2S content when H_2S removal is employed. Thus, data on the concentrations of mercaptans and COS in refinery gases are difficult to obtain although industry experts claim that the concentration of these gases in refinery fuels is generally higher than in most natural gas streams.

TABLE 2. COMPOSITION OF VARIOUS NATURAL GASES[8]

Component	Composition, mole %, of gas from Rio Arriba County, N.M.	Terrell County, Texas	Stanton County, Kansas	San Juan County, N.M.	Olds Field, Alberta, Canada	Cliffside Field, Amarillo, Texas
Methane	96.91	45.64	67.56	77.28	52.34	65.8
Ethane	1.33	0.21	6.23	11.18	0.41	3.8
Propane	0.19		3.18	5.83	0.14	1.7
Butanes	0.05		1.42	2.34	0.16	0.8
Pentanes and heavier	0.02		0.40	1.18	0.41	0.5
Carbon dioxide	0.82	53.93	0.07	0.80	8.22	
Hydrogen sulfide		0.01			35.79	
Nitrogen	0.68	0.21	21.14	1.39	2.53	25.6
Helium						1.8
Total	100.00	100.00	100.00	100.00	100.00	100.00
Total sulfur, grains/100 ft^3	0	6.3	0	0	22,525	
Classification						
wet				x		
dry	x	x	x		x	x
sweet	x		x	x		x
sour		x			x	
Gross heating value, Btu/ft^3	1,010	466	938	1,258	807	825
Specific gravity	0.574	1.0777	0.733	0.741	0.882	0.711

TABLE 3. COMPOSITION OF NATURAL GASES* (1972-73 Data) - Mole %

	Gas Sample No. 1	Gas Sample No. 2	Gas Sample No. 5	Gas Sample No. 6
Carbon dioxide	43.40	1.27	4.4	1.6
Nitrogen	0.50	0.94	8.7	1.6
Hydrogensulfide	0.01	0.37	10.6	0.6
Methane	56.00	91.16	59.93	83.5
Ethane	0.09	4.05	7.7	8.0
Propane	0	1.20	4.1	3.3
Isobutane	0	0.13	1.3	0.3
N-butane	0	0.36	2.1	0.8
Iso-pentane	0	0.10	0.6	0.1
N-pentane and heavier	0	0.42	0.6	0.2
Total	100.00	100.00	100.00	100.00
Btu/cft	570	1060		
Total sulfur gr/100 cu ft.	10	200	NA	
Specific gravity	0.975	0.622		

* These data were reported by AMOCO, Shell and Exxon in response to BCL requests. However, it should be noted that there are wells in the U.S. and Canada that contain greater than 50 percent H_2S by volume.

TABLE 4. SULFUR COMPOUNDS IN UNTREATED NATURAL GAS

Sulfurous Components	Gas Sample 1 grams*/ 100 s cu m	Gas Sample 2 grams/ 100 s cu m	Gas Sample 3 grams/ 100 s cu m	Gas Sample 4 grams/ 100 s cu m	Gas Sample 5 grams/ 100 s cu m	Gas Sample 6 grams/ 100 s cu m
Hydrogen sulfide (H_2S)	153	76	2	24,905	29,213	21,369
ppmv of H_2S	1044	519	14	170,026**	199,437**	146,000**
Mercaptans (RSH)	21	14	0.12	627**	735**	973**
Sulfides (COS etc)	7	5	0.04	188	220	893
Residual sulfide (S)	4	2	0.01	105	121	146
Total sulfur	185	97	2.17	25,825	30,289	23,381
CO_2 (mole %)	1.5	0.71	2.42	NA	NA	NA

* Multiply given values by 0.43665 to obtain grains/100 scf.

** Such high concentrations are not common in natural gas streams. These concentrations of sulfur compound definitely are much higher than those of refinery fuel gas. As pointed out elsewhere, about 2 percent of U.S. natural gas is sour and less than 2 to 3 percent of the sour gases contain high sulfur compound levels presented in this table.

(Source: Mr. Neal, Petroleum Analytical Laboratory Service, Odessa, Texas)

TABLE 5. ANALYSES OF CATALYTIC CRACKER GAS*

	Mole %
Carbon dioxide	1.24
Hydrogen sulfide	6.38
Carbonyl sulfide	-
Hydrogen	44.86
Methane	32.17
Ethane and heavier	14.35
Water	1.00
Temperature C (F)	60 (140)
Pressure, atmospheres (PSIG)	5.5 (80)

*** Not a typical analyses. See text, page 18.**

(Source: Official Communication dated January 4, 1972 from David C. Parnell, Chief Process Engineer, Ford, Bacon and Davis Texas Inc., to Richard K. Burr, U.S. EPA, RTP, NC 27711)

Comparison of Refinery and Natural Gases

The most important differences related to the design of sulfur recovery units from the two gases are

(1) Presence of heavy hydrocarbons including aromatics in the refinery gases which tends to form a somewhat black sulfur instead of the more readily marketable yellow sulfur in the sulfur recovery step.

(2) The refinery gases are usually at atmospheric pressure and higher than ambient temperature. Natural gas is at higher pressure (>25 atm. depending on the stages of separation) and a lower temperature. These factors contribute to the ease of processing natural gas during the H_2S removal step. The absence of heavy hydrocarbons in natural gas helps in recovering pure yellow sulfur.

(3) Other differences are that refinery gases contain cracked products (gum-forming olefins) and are more likely to contain sulfur compounds like carbonyl sulfide, mercaptans, etc., as discussed on page 18.

To generalize on these differences and summarize how they affect the design of sweetening and sulfur-recovery units is not practical because there are far too many variables involved in the design. However, it cannot be too strongly emphasized that design of treatment units for refinery gases requires more careful tailoring to individual gas compositions. This is not to imply that design of natural-gas treatment units is highly standardized.

III. MAJOR DESULFURIZATION PROCESSES IN OIL AND GAS PROCESSING

The natural gas industry has to sweeten (remove H_2S from) both the gas and sometimes the liquified gases such as propanes, butanes, etc. Available sweetening processes employ physical, chemical and a combination of separation techniques. Thus, a confusing array of gas and liquid sweetening processes is in use. These are discussed below under two headings: (1) gas sweetening processes and (2) liquid sweetening processes.

Gas Sweetening Processes*

These can be grouped under five types: (1) the Amine Processes, (2) the New Amine Processes, (3) Carbonate Processes, (4) Physical Absorption Methods, and (5) Solid-Bed Sweetening Processes. Most of these processes remove both the H_2S and CO_2 from the natural gas to produce an "acid gas" rich in H_2S and CO_2. Further processing of this acid gas is necessary to produce sulfur. This is discussed under sulfur production processes.

Also, processes that combine H_2S removal and direct sulfur production are used selectively. Examples of such processes are the Stretford process used in the U.S. and the Giammarco-Vetricoke Process (GV) in use primarily in Europe.

A summary of the essential features of all these processes is presented in Table 6. A brief discussion of each process type follows. Detailed discussion and flow diagrams are presented in Appendices A, B and C.

Amine Processes (Including New Amine Processes)

Although at least five different types of amine processes have been developed, only three (MEA, DEA, and sulfinol) have gained wide usage in the industry. Of these processes, the MEA and DEA (used chiefly in refineries), are two of the oldest gas-sweetening processes which are still used in over 300 installations.

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* There is considerable overlap in processes used for gas and liquid sweetening.

TABLE 6 . SUMMARY OF MAJOR GAS

Process Name (Process Applicability)	Process Mechanism	Process Conditions: Temp., C	Pressure, atm	Solution Concentration, percent	Regeneration	Product Form
Amine Processes						
Monoethanolamine (MEA)	Liquid chemical absorption (acid-base reaction)	30-55	1-70	15-20% in water	In a steam stripper column	H_2S gas
Diethanolamine (DEA)	Liquid chemical absorption in an aqueous solution	30-55	1-70	15-20% in water	By steam stripping	H_2S gas
New Amine Processes						
Diglycolamine (DGA) or Flour Econamine (sour gas	Improved liquid chemical absorption with alkanolamine	30-55	1-70	Up to 60% in water	Yes	H_2S gas
Shell sulfinol (gas and liquid sweetening)	Liquid chemical absorption plus physical solution of H_2S in sulfolane	30-50	1-80	Highly variable	Yes	H_2S gas
SNPA-DEA Societe Nationale des Petroles d'Aquitaine (sour gas)	Same as DEA process but the DEA concentration is high in this improved version	30-55	1-70	20-30% in water	Yes	H_2S gas
Shell ADIP (Gas and liquid sweetening, mostly in refineries)	Regenerative absorption in aqueous solvent amine (diisopropanol amine)	25-40	1-80	25 to 30% in water	Pressure reduction plus stripping	H_2S gas
Carbonate Processes						
Benfield (Benson and field invention) Benfield Corporation, Pittsburgh Pa. (Natural and synthesis gas)	Activated (promoted) hot K_2CO_3 process	25-200	7-300	20 to 35%	By steam stripping	H_2S gas
Catacarb (sour gas)	Catalyzed hot K_2CO_3 Process with corrosion inhibitor	55-130	10-70	Not known	Steam plus gas stripping	H_2S gas
Physical Absorption Processes						
Selexol (Allied Chemicals) (gas and liquid sweetening)	Physical absorption of CO_2 and H_2S in dimethyl ether of polyethylene glycol (DMPEG)	5	20-80	5 to 10% in water	Yes, by stage flashing and reheat	H_2S gas
Rectisol Lurgi Mineraloltechnik GMbH (syngas)	Removes CO_2, H_2S, NH_3, HCN and other impurities from crude gases from coal gasification, etc.					
Solid Bed Sweetening Processes						
Molecular sieve (sodium aluminum silicate) Union Carbide Corporation, Linde Division (914) 345-3196 (Gas and liquid stream with water, H_2S, CO_2)	Physical absorption	10-40	5-100	Varies	Heat	H_2S gas
Simultaneous H_2S Removal and Sulfur Production Processes						
Giammarco Vetrocoke-sulfur (sour gas)	Good process, but use of arsenic salts in the absorbing solvent is not acceptable in the U.S.					
Stretford-ADA vandate (sour gas)	Dissolution in aqueous solution of sodium carbonate, sodium vandate, and anthraquinone disulfonic acid (ADA)	58	0-100	Varies	Yes	Pure sulfur
Sulfreen (SNPA/Lurgi) The Ralph M. Parson (Gas containing SO_2)	Although this process converts H_2S to sulfur, it is essentially an extension of the Claus reaction.					

AND LIQUID SWEETENING PROCESSES

Number of Units in Operation in the U.S.	Selectivity for H_2S in $H_2S + CO_2$ Rich Feed	Advantages (Also see text)	Disadvantages	Utilities Requirements
>300 units mostly in refineries	Nonselective	Rapid reaction with acid gas (H_2S, CO_2, etc.)	More difficult to regenerate. Higher utility costs	Depends on feed and/or CO_2, H_2S concentration
>300 units mostly in refineries	Good for H_2S	0.2 mole acid gas/mole of MEA		
56 x 10^6 S Cu m in operation in natural gas	--		Currently DGA is in short supply	
58 (HG), widely accepted in natural gas, refinery gas, coke oven gas operations. 18 in Canada	Excellent up to 50% CO_2 can be retained in gas	-Removes 90% of all mercaptans with no additional burdens. -High solution loading -Excellent ease of operation -Skid mounted units for small gas operations available	Absorbs heavy aromatics from the gas	Very low. Lower than MEA and DEA. See Table next page
None in the U.S. 12 in other countries	None	Lower utility requirements		low
30 Widely accepted for refinery gases in Europe. Many in Europe	Good selectivity achievable	Well demonstrated process for refining gases No corrosion problems Applicable to liquid hydrocarbons, synthetic gas, etc. Flexible operating conditions	--	Low steam consumption
20 in natural gas >200 in NH_3 plants, etc.	Possible	The higher the pressure the better Lower solubility of HC	MEA is better for low pressure (100 psi) Must have at least 20% total acid gas and must be CO_2	Low steam consumption
66 units total	Possible	Low cost of materials	--	--
3, more under construction	Moderate selectivity for H_2S is possible	Can handle both high and low CO_2 and H_2S gases. Lower capital and operating costs are claimed by developers	Can treat high pressure gases only (>20 atm)	Very low compared to MEA Hot K_2CO_3 processes

Not used in natural gas industry but is mentioned here to emphasize that it is a major process.

12 in gas 30 in LNG	Excellent for H_2O and H_2S	Easy to operate and very useful for LNG purification	Off gas from regenerator is too lean in H_2S for a Claus plant. Hence concentrator is needed.	--

Hence this process is not likely to be used in the U.S.

55 units total	Completely selective to H_2S	No tail gas hence no H_2S emissions

Therefore it is discussed in detail under "Tailgas Cleaning Processes".

Detailed process descriptions are available in literature[10] and Appendix A. Essentially, the principle used is the chemical reaction of H_2S and CO_2 with amine. In recent years the Sulfinol and other improved processes are tending to replace the not-so-selective MEA and DEA processes. A comparison of some operating data for the MEA, DEA, DGA, and Sulfinol processes are presented in Table 7.

Carbonate Processes

Most of the carbonate processes were designed to remove CO_2 (rather than H_2S) from the gas. The principle used is that CO_2 (and to a lesser extent H_2S) has a high affinity for potassium carbonate (K_2CO_3) and hence, K_2CO_3 can be used to remove CO_2 and H_2S from a mixture of gases according to the following reactions.

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3 \quad \text{and}$$

$$K_2CO_3 + H_2S \rightleftharpoons KHS + KHCO_3 \quad .$$

Since the salt formation in both reactions is high, high temperatures are employed to keep the salt in solution. Thus, the process is called hot carbonate process.

The hot carbonate process has been successfully utilized for bulk removal of CO_2 and incidental removal of small concentrations of H_2S. The process will not work if only H_2S but no CO_2 is present. The process has the advantage that both carbon disulfide (CS_2) and carbonyl sulfide (COS) can be removed without significant solution degradation. Carbonyl sulfide, for example, will hydrolyze as follows.

$$COS + H_2O \longrightarrow CO_2 + H_2S \quad .$$

The CO_2 and H_2S are removed as per reactions described earlier.

TABLE 7. COMPARISON OF CIRCULATION RATES AND REBOILER STEAM RATES FOR VARIOUS TREATING PROCESSES[10]

ITEM	Gas "A"	Gas "B"	Gas "C"	Gas "D"	Gas "E"
Contactor Pressure, psia	1,000	1,000	1,000	1,000	1,000
Feed Gas Temp., °F	110	110	110	110	110
Feed Gas Flow (Dry), MMSCFD	100	100	100	100	100
Feed Gas Composition, Mol %					
H_2S	0.65	20.1	20.10	51.5	0.10
CO_2	8.73	2.0	2.00	3.5	18.00
N_2	2.37	1.4	1.40	8.6	0.70
C_1	87.90	71.5	63.01	25.8	80.94
C_2	0.35	2.0	8.43	5.8	0.17
C_3		1.7	3.71	3.2	0.05
C_4		1.1	0.82	1.6	0.04
C_{5+}		0.2	0.53*		
TOTAL	100.00	100.00	100.00	100.00	100.00
COS, Grs/100 SCF	3.0	7.3	7.3	8.4	
RSH, Grs/100 SCF	2.1	1.5	1.5	3.1	
H_2S/CO_2 Ratio	0.0744	10.05	10.05	14.71	0.0056
Sweet Gas H_2S Content, Grs/100 SCF	< 0.25	<0.25	<0.25	<0.25	<0.25
Sweet Gas CO_2 Content, Mol %	< 1.0	<1.0	<1.0	<1.0	2.0**
Sweet Gas Total Sulfur, Grs/100 SCF	< 1.0	<1.0	<1.0	<1.0	< 1.0
Solution Circulation Rate, gpm @ 110°F					
Sulfinol (Composition Varies)[7]	1,483	1,748	1,790	2,366	2,167
MEA (15 wt. % MEA)	2,170	5,115	5,115	12,730	4,190
DEA (25 wt. % DEA)	1,272	2,997	2,997	7,460	2,455
DGA (65 wt. % DGA)	1,277	3,010	3,010	7,490	2,465
Solution Net Pickup, SCF Acid-Gas/Gal					
Sulfinol Sol'n.	4.39	8.78	8.57	16.14	5.24
MEA Sol'n.	3.00	3.00	3.00	3.00	3.00
DEA Sol'n.	5.12	5.12	5.12	5.12	5.12
DGA Sol'n.	5.10	5.10	5.10	5.10	5.10
Reboiler Steam Rate, #/HR					
Sulfinol Sol'n.[7]	69,740	111,440	125,960	156,000	99,600
MEA Sol'n.	143,200	337,590	337,590	840,180	276,540
DEA Sol'n.	87,770	206,790	206,790	514,740	169,400
DGA Sol'n.	91,950	216,720	216,720	539,280	177,480
Reboiler Steam Rate, #/Gal. Sol'n.					
Sulfinol Sol'n.	0.78	1.06	1.17	1.10	0.77
MEA Sol'n.	1.10	1.10	1.10	1.10	1.10
DEA Sol'n.	1.15	1.15	1.15	1.15	1.15
DGA Sol'n.	1.20	1.20	1.20	1.20	1.20

* Includes 0.02 Mol. % aromatics.
** 2.0 mol. % CO_2 for Sulfinol; < 1.0 mol. % for all other processes.

(Courtsey: Campbell Petroleum Series and Dr. R. N. Maddox)

Liquid-Sweetening Processes

Liquid sweetening is also widely practiced in the natural-gas processing industry.

Many of the gas-sweetening processes discussed previously also serve to sweeten liquid hydrocarbons. Examples of such processes are:

(1) Molecular Sieve Process

(2) MEA Process (plus caustic wash)

(3) Adip Process.

The Molecular Sieve process is particularly suited to the simultaneous drying and removal of H_2S and CO_2 and is widely used. Maddox[10] describes other processes used in the sweetening of gasoline fractions (hence, not used in natural-gas processing). These are the Merox Process, Caustic Wash, Copper Sweetening, etc.

Environmental Effects of Liquid Sweetening

Atmospheric emissions and other environmental burdens are not significant because, although the volume of plant liquids treated is significant, the total amount of sulfur removed is small.

IV. DESCRIPTION OF LESSER KNOWN SULFUR(H_2S) REMOVAL PROCESSES

Many factors need to be considered when selecting a process for a given sweetening application. These include:

(1) The types of impurities to be removed from the gas stream.

(2) The relative concentration level of these impurities and the degree of removal desired.

(3) The acid gas selectivity required, if any. (Selectivity for H_2S vs CO_2)

(4) The volume of gas to be processed and the temperature-pressure conditions at which the gas is available.

(5) The feasibility and desirability of sulfur recovery.

(6) Relative economics of the suitable processes.

Acid gas constituents present in most natural gas streams are hydrogen sulfide and carbon dioxide. Many gas streams, however, particularly those in a refinery or for manufactured gases, may contain mercaptans, carbon disulfide and/or carbonyl sulfide. Any of these constituents present in the gas stream will lead to irreversible reactions, degradation of sweetening solution or non-removal of the acid gas constituent which may cause many processes to be ineffective or economically unattractive.

The level of acid gas concentration in the sour gas is an important consideration for selecting the proper sweetening process. Some processes are applicable for removal of large quantities of acid gas; however, many of these processes will not sweeten to pipeline specifications. Other processes have the capacity for removing acid gas constituents to the parts per million range - although some are applicable only to low concentrations of acid gas constituents in the sour gas to be treated.

The selectivity of a sweetening agent is an indication of the degree of removal that can be obtained for one acid gas constituent as opposed to another. There are sweetening processes which display rather marked selectivity for one acid gas constituent. In other cases there is no selectivity demonstrated and all acid gas constituents will be removed. There are processes for which operating conditions can have a marked effect

on the selectivity exhibited. Some sweetening agents absorb relatively large amounts of hydrocarbons while others are much more selective for the acid gas constituents.

Only rarely will natural gas streams be sweetened at low pressures. Moreover, there are processes which are unsuitable for removing acid gases under low pressure conditions. Other processes are adversely affected by temperatures much above ambient. Some processes lose their economic advantage when large volumes of gas are to be treated.

The major processes described earlier have gained acceptance because among other reasons they are very flexible in their application. However there are numerous not-so-widely used processes examples of which are: (1) the Purisol Process licensed by Lurgi, (2) the Iron Oxide (sponge) Process, (3) Many of the carbonate processes including the Giammarco-Vetrocoke Process, and (4) the Fluor solvent process licensed by the Fluor Engineers and Constructors. All these processes, used more in Europe than in the U.S., show high selectivity for either H_2S or CO_2. For example, the iron oxide process is completely selective to H_2S; thus a gas from which only H_2S needs to be removed, other conditions favoring, could be treated by iron sponge process. Basically therefore, the lower cost and selectivity determine the justification for the minor processes. It is emphasized that to generalize on which process to employ for a general range of input and output of H_2S concentration in natural gas is almost impossible. Every gas stream will have to be analyzed with reference to as many processes as necessary to derive the factors required to make a proper process selection. This is a major process selection project for each gas well or combination of wells in a field.

Minor Desulfurization (H_2S Removal) Processes

A brief description of the four lesser known processes is provided below and detailed flow sheets are presented in Appendix B. The four processes are listed in Table 8 with possible reasons for the choice of each process in a given processing situation.

TABLE 8. LISTING OF LESSER KNOWN GAS DESULFURIZATION PROCESSES

Process Name and Licensor/Seller	Approximate Reasons for the Choice of Process	Number of Units Installed
PURISOL Lurgi Mineral GMBH	- Good selectivity for H_2S or CO_2 can be achieved - Low temperature (ambient) operation - Low circulation rate for a given situation - CO_2 removal by pressure let down - Excellent solvent stability - Nontoxic fumeless operation	2 Units in Natural gas outside the U.S. None in U.S. in natural gas 2 units in hydrogen manufacture in the U.S.
IRON SPONGE (OXIDE) Sold by many including National Tank Company, Tulsa, Oklahoma (918) 663-9100	- Removes efficiently trace amounts of H_2S in gas - Batch process has low investment and operating costs. Infinite turndown capability - H_2S removal independent of gas pressure - Easily installed (wood chips coated with iron oxide is packed in any available cylindrical column). - The used iron oxide is thrown away as solid waste or burned - Very low capital costs ($20,000) for a system with 10 grains/100 scf H_2S at 2 million scfd of gas.	More than 200 batch units in operation. However, the construction is so simple and costs so low that builders cannot justify maintaining record of installations
FLUOR SOLVENT Fluor Engineers and Constructors	- Low solvent loss due to low vapor pressure of polypropylene carbonate - High capacity solvent, which absorbs acid by gas by physical solution, permits solvent regeneration simply by pressure let down of rich solvent, usually without the application of heat. - Solvent breakdown rate is virtually zero - Carbon steel is used in construction - The process is favored when the combined partial pressure of $CO_2 + H_2S$ is > 5 atm; and when the heavy hydrocarbons are low.	7 plants in natural gas 1 plants in ammonia production 2 plants in hydrogen production

TABLE 8. (Continued)

Process Name and Licensor/Seller	Approximate Reasons for the Choice of Process	Number of Units Installed
GIAMMARCO-VETROCOKE (Power-Gas Ltd.)	- Treating costs about half the costs of most other processes (hot carbonate, MEA). - Low capital costs - Low corrosion of G-V plants - No solution degradation - Process not applicable if H_2S content is above 1-5 volume present - Treated gas has low H_2S content of 1 ppm (0.06 gr/100 scf) - Process can operate at pressures as low as atmospheric and temperatures up to 150 C.	One plant in natural gas in the U.S. (West Texas) Used mostly in Europe. Use of the process in the U.S. is not likely to increase because of the arsenic used in absorption solution.

Purisol Process

Detailed flow sheet, process description and operating conditions are presented in Appendix B. The process is applicable to the removal of acid gases (H_2S + CO_2) from Syngas (synthetic gas) and natural gas streams using physical absorption in N-Methyl-Pyrrolidone (NMP).

Iron Sponge (Oxide) Process

Detailed flow sheet, process description and operating conditions are presented in Appendix B. This process is well suited for removal of H_2S when it is the only undesirable component of natural gas. The process does not generate atmospheric pollutants because the sulfur formed in the iron oxide bed can be disposed of in a landfill, providing that a suitable landfill site away from water ways (both surface and underground) is available.

Fluor-Solvent Process

Detailed flow sheet, application and process description are presented in Appendix B. The process is excellent for the removal of high concentration of acidic gases (when the combined partial pressure of CO_2 + H_2S is about 5 atmospheres or higher). The processing arrangement can be modified to suit the degree of purification required for both H_2S and CO_2. Solvent regeneration is inexpensive and solvent carrying capacity is high because of the sufficient free refrigeration obtained by expansion of the acidic constituents. The process does not require special or exotic materials of construction.

Giammarco-Vetrocoke Sulfur Process

Detailed flow diagram, application, process description and operating conditions are presented in Appendix B. The process produces

sulfur as a precipitate directly by continuous scrubbing of H_2S with an alkali arsenates and arsenites solution.

The main drawback of the process for gaining acceptance in the U.S. is the use of arsenite compounds in the scrubbing solution. In addition, if both CO_2 and H_2S are present, two separate treating units are required. The process is used widely in Europe and other countries.

Level of Sulfur Compounds in Treated Natural Gas Attainable by Various Processes

The level of sulfur compounds attainable by the 18 processes described earlier is summarized in Table 9. Obviously, there are data gaps. It should be noted that the extent of removal of H_2S and other compounds depends on the partial pressure of these compounds and the careful design of the process to attain that level.

In general, the gas industry can confidently state the specific level of H_2S attainable in the product natural gas. However, since the gas industry was not particularly required to concern itself about the concentration of other sulfur compounds in product natural gas, insufficient exact data on the levels of COS, CS_2, and RSH exist. Recommended levels of sulfur compounds as maximum permissible concentrations in natural gas sold as industrial and residential fuel are presented in Table 10.

Based on the fact published by the AGA* that about 8 percent of the gas is sold to industry and commerce, a 64-ppm total sulfur level (4.0 gr/100 scf) would have resulted in a sulfur emission of 12 MT/D by natural gas combustion during 1973. This quantity of emission (0.009 million MT/Y as SO_2) is very insignificant in comparison with national SO_2 emission data presented in Table 16. The insignificance of this quantity will be more pronounced due to the area source nature of the emissions.

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* GAS FACTS - 1971 data, American Gas Association, Arlington, Virginia.

TABLE 9. APPROXIMATE LEVEL OF SULFUR COMPOUNDS IN TREATED NATURAL GAS WITH VARIOUS PROCESSES

Process Name	Level of Sulfur Compounds In Treated Natural Gas (ppm)[a]					Source of Information
	H_2S	COS	CS_2	RSH	Total Sulfur[b]	
Major absorption mode used in removal	Physical	Chemical	Chemical	Physical		
MEA (aqueous)	<4	<2	<2	50%[c]	<10[b]	Industry Expert
DEA (aqueous)	<4	<5	<5	60%[c]	10-16[b]	"
DGA	<4	(d)	(d)	(d)	(d)	"
Sulfinol	<4	<2.0	<1	>90%[c] Removal	<10	"
SNPA-DEA						
ADIP	<4	<2.0	<1	50%[c]	<10[b]	"
Benfield	<4	<1	<0.5	60%[c]	<10	"
Catacarb						
Selexol	<4					
Rectisol						
Mol-sieve	0.8				1.0	Union Carbide Bulletin F-86
GV-Sulfur	<2					
Stretford	<0					
Sulfreen						
Purisol	<0.4					
Ironoxide	<0.1					
Flour Solvent	<0.4					
GV-Sulfur	<0.4					

(a) Blank spaces signify data not available.

(b) Depends on inlet mercaptan (RSH) levels.

(c) Indicates percent RSH removed.

(d) No definite levels can be specified. Mr. Dingman (see Appendix F) is of the opinion that the feed gas conditions and composition should be known to arrive at levels of these compounds that can be attained.

TABLE 10. RECOMMENDED MAXIMUM CONCENTRATION OF SULFUR COMPOUNDS IN NATURAL GAS SUPPLIED TO GAS TRANSMISSION SYSTEMS FROM NEW PROCESS PLANTS(a)

Name of Compound	Maximum Concentration, ppm
Hydrogen sulfide (H_2S)	16
Carbonyl sulfide (COS)	(b)
Carbon disulfide (CS_2)	(b)
Mercaptans (RSH)	(b)
Total sulfur (S)	64(c)

(a) These concentration limits apply to new gas processing plants only.

(b) The allowable concentration of COS, CS_2, mercaptans, and other sulfur compounds shall be such that the total sulfur content of the treated gas (which determines the ambient SO_2 emissions) shall not exceed 64 ppm (4 grains/100 scf).

(c) The intent of this limitation on total sulfur is to limit sulfur emissions to atmosphere when the natural gas is burned as fuel. Therefore, when the same gas processing facility produces sour and sweet gases both feeding to a common transmission system, the recommended total sulfur limitation may need adjustment. Such adjustment shall include the permitting of a higher total sulfur concentration in treated sour gas such that its admixture with the sweet gas at the pipeline inlet will not result in a total sulfur greater than 64 ppm in the gas mixture. Also, in those rare cases when the concentration of mercaptans in sour gas exceeds 400 ppm, the allowable total sulfur limit shall be adjusted to account for the fact that the best control technology limits mercaptan removal to 90 percent of inlet mercaptan level.

V. COMPARATIVE DESCRIPTION OF SULFUR REMOVAL AND PRODUCTION PROCESSES IN NATURAL GAS AND REFINERY GASES

The choice of processes used in desulfurization of natural and refinery gases is based on the following parameters.

(1) Gas composition

(2) Gas volume

(3) Required degree of removal of undesirable constituents in the gases

As discussed earlier, there are 14 major processes and at least four minor processes in use for the removal of H_2S in the natural gas processing industry. Generally, the product from these 18 processes is an acid gas (a mixture of $H_2S + CO_2$) which is further processed in a sulfur plant to pure sulfur which is sold when a ready market is available. The tail gas from the sulfur plant may need to be further treated by use of one of the many tail gas treatment processes which have been recently developed. Examples of tail gas treatment processes are: (1) the IFP, (2) the Wellman-Lord SO_2 removal process, (3) the Clean air process, (4) the Beavon process, and (5) the SCOT process, etc.

A recent Battelle study[11] indicates that processes for removal of H_2S from refinery fuel-gases are: (1) the Shell Adip, (2) Girdler's Girbotol*, (3) DEA, (4) Fluor Econamine, and (5) the Shell phosphate process. Not included among these five fuel-gas treatment process is the Stretford process which is a direct oxidation process for removing H_2S to obtain sulfur as the product directly.

The four processes (Adip, MEA, DEA, and Econamine) which have common applicability to both the natural gas and the refinery gas desulfurization needs have been described earlier in Table 8 and Appendices A and B. An industry expert is of the opinion that the Shell phosphate process is not

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* Same as MEA Process.

in the current list of processes readily offered for licensing. However, this process will be sold if specific demand exists which happens in certain unusual situations. The older units using this process are still working well.

It appears therefore that the process for H_2S removal used in the natural gas industry and in the refinery fuel gas treatment are not significantly different. However while the process choices available for natural gas industry are from more than 20 processes, the refinery gases have a limited choice, the reasons for which are explored in this chapter.

Factors in the Selection of H_2S Removal Processes

The parameters in the choice of processes listed earlier can be covered under three factors which govern the selection of processes for hydrogen sulfide removal from refinery fuels.

Solubility of Organic Components of the Fuel Gas in Absorption Solvent

Natural gas has a much lower concentration of heavy hydrocarbons (less than 1 percent of heptanes and heavier) than refinery fuel gases. As an example, a catalytic-cracker gas contains more than 10 percent of heavy hydrocarbons which tend to be soluble or otherwise be held in the absorption solvent used in the H_2S removal process. The Shell Sulfinol process is a typical example in which the solvent (sulfolane, di-isopropanol amine, and water) tends to absorb heavy hydrocarbons from the feed gas, especially the aromatics.

By contrast, the solvent in the Shell ADIP process (di-isopropanol amine) and the DEA process (diethanolamine) have a very low solubility for almost all hydrocarbons because among other reasons, the solvents are used as aqueous solutions (Ca 75 percent water by weight). This is one of the reasons for the very wide use of ADIP and DEA in cleaning of refinery fuel

gases. Very few solvents have low solubility for heavy hydrocarbons while at the same time maintaining good desulfurization ability. The MEA, DEA, and ADIP processes appear to be about the only processes that are being widely used in refinery fuel gas cleaning for this reason.

Presence of Sulfur Species Other Than H_2S in Untreated Gas

In general, the concentration of non-H_2S sulfur species is higher in refinery-fuel-gas streams than in natural-gas streams because the refinery cracking reactions generate these sulfur compounds*. Consequently, refinery-fuel-gas streams tend to severely degenerate certain solvents used in H_2S removal. Such degeneration is generally not a serious problem in natural-gas streams. The Sulfinol process, quite widely used in natural-gas treating, is substantially immune to solvent degeneration[10]; the cost of solvent, however, is high. The MEA solvent is subject to heavy degeneration by carbonyl sulfide (COS), etc., and hence, is seldom used in refinery-gas cleaning where the concentration of COS, etc., in the gases is quite high; DEA and ADIP are not subject to degradation by COS and are therefore favored for refinery-fuel-gas cleaning. This is one additional factor considered in process selection.

Required Degree of Removal of Sulfur Compounds

Pipeline companies have set the H_2S level in natural gas by the quarter-grain or one-grain concept (0.25 grains or 1.0 grain H_2S per 100 scf equivalent to 6 or 23 mg/s cu m). However, no such strict limits for H_2S content exist for refinery fuel gases because they are burned as plant fuel on site and do not need to be piped to customers. Further, the total sulfur level in natural gas is usually also limited by sales agreements for natural gas to about 10 to 20 grains/100 scf. By contrast, the total sulfur level in refinery gaseous fuels can be as high as 100 grains/100 scf and the H_2S level can also range from 1 to 50 grains/100 scf. These facts tend

* Carbonyl sulfide (COS), carbon disulfide (CS_2), etc.

to favor the selection of desulfurization processes that have low overall cost and lower sulfur removal efficiency for refinery-fuel treating. The Shell ADIP process has the ability to be designed for both low- and high-H_2S removal. However, the need for more effective removal of sulfur compounds like COS, CS_2, etc., is greater in natural-gas treatment. Thus, the sulfinol for example has a greater applicability to natural-gas treatment.

Other Factors in Process Selection

The extent of carbon dioxide present in natural-gas streams is also a factor in the selection of the gas-treating process. Some natural-gas streams contain very high (50 percent or more) concentrations of CO_2 and low concentrations of H_2S which favor the use of a modified (promoted) carbonate process. Similarly, if the refinery fuels contain high CO_2 levels, the selected cleaning process will have to deal with removal of the high CO_2 levels. Outside the U.S., the GV-carbonate removal process is widely used for this situation.

The above factors do not cover all of the aspects involved in the selection of a process. Process selection is an expert area and detailed process engineering, design, and economic analyses must precede the selection of a process.

Methods of Sulfur Production in Natural and Refinery Gas Applications

Two different principles of sulfur production from H_2S are in current use: (1) direct vapor phase oxidation-reduction and (2) liquid phase absorption-oxidation.

Direct Vapor Phase Oxidation Principle

The well known Claus process employs this principle of oxidation-reduction as follows:

$$H_2S + 3/2\ O_2 \longrightarrow H_2O + SO_2 \quad \text{(oxidation)}$$

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S \quad \text{(Reduction)}$$

$$\text{overall,} \quad 3H_2S + 3/2\ O_2 \longrightarrow 3H_2O + 3S$$

If the acid gas (or feed to Claus plant) contains hydrocarbon compounds, the following undesirable reactions also take place[10].

$$CH_4 + SO_2 \longrightarrow COS + H_2O + H_2$$

$$CO + S \longrightarrow COS$$

$$CO_2 + H_2S \longrightarrow COS + H_2O$$

$$CH_4 + 2S_2 \longrightarrow CS_2 + 2H_2S$$

$$2CO + S_2 \longrightarrow CS_2 + CO_2$$

Carbonyl sulfide (COS) and carbon disulfide (CS_2) are the undesirable constituents contributing to tail gas sulfur.

It also is quite likely that in the presence of hydrocarbons, the following reaction will occur

$$3CH_4 + 3/2\ O_2 \longrightarrow 4H_2 + CO + 2C + 2H_2O.$$

This reaction can use up the air supply as well as blind the catalyst with carbon soot.

The Claus plant has found wide acceptance in both the refinery and natural gas industries. The choice of the Claus plant is simply a function of the availability of enough acid gas feed to the unit. Eighty-four Claus units (Appendix I) are installed in natural-gas processing with a total capacity of 6250 MT/D[9]. The number of Claus units in refinery-gas sulfur recovery is about 200, with a total production capacity of 8000 MT/D[11].

Detailed description of a Claus plant with three catalytic stages of conversion is presented in Appendix C.

Claus Sulfur Plant Capacity VS Production Rate

According to the data[9] presented in Appendix I (List of Claus Plants in Natural Gas Processing), as of April, 1973, there were 84 sulfur production units in natural gas processing with a total design capacity of 6,250 MTD. However eight of these plants with a total capacity of 660 MTD were stand-by units. Further, available production data for 1972 indicate that in most cases, the actual production was about 50 percent of design capacity. This may be due to the reduced gas output coupled with initial optimistic overdesign of the Claus units.

The sulfur production data (2443 MT/D) reported in a later Section (Table 14) is in reasonable agreement with estimated data from Appendix I* assuming average production to be about 50 percent of plant design capacity.

There are 31 Claus plants with design capacity greater than or equal to 50 MT/D. If 50 MT/D is arbitrarily chosen as the cut point at which tail gas cleaning requirement would be deemed necessary then a total of 35 tail gas units could be expected in natural gas processing industry. The rationale for chosing a 50 MT/D plant as the cut off point is that 94% Claus plant efficiency, the tail gas unit will have at least 3 MTD of sulfur production. This will be discussed in greater detail in a later Section.

Sulfur Recovery Efficiency of Claus Plants. A considerable amount of study on the present and potential efficiencies of Claus plants has been conducted by the companies connected with sulfur production and recovery in the Province of Alberta, Canada. It is only natural that such study has been initiated in the Alberta area which is the world's leading sulfur production center.

Rankine[2] et al contend that theoretical calculations and field scale experiments together clearly demonstrate the potential of the Claus

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*(6250-660)/2 = 2795 MT/D = (Total Claus plant capacity - Capacity of standby units) x (Plant utilization factor of 0.5). This "reasonable" agreement implies that almost all of the Claus plants in natural gas processing are listed in Appendix I.

process to achieve efficiencies well in excess of the present of 90-97 percent. In their opinion more research should be directed to the exploitation of the Claus plant's potential for increased efficiency. On the contrary, so far, most of the research effort has been directed towards development of new process intended to augment Claus plant efficiencies.

The study model[2] has led to the definition of several criteria for optimum Claus plant performance; namely

(1) Each sulfur condenser should operate at about 260°F which provides a margin of about 20°F above the freezing point of sulfur.

(2) Mist elimination equipment should be utilized in interstage sulfur condensers as well as in the final condenser.

(3) Methods of reheat which introduce sulfur compounds into the main gas stream should be avoided. This is in adherence to the principle that optimization implies all sulfur compounds are introduced as far upstream in the plant as possible.

(4) The operation of each converter should be adjusted so that the actual and dew point temperatures converge at the converter outlet.

They conclude that these criteria have not been generally adhered to in the design and operation of existing Claus plants. Finally, the thermodynamic recoveries from a four stage Claus plant processing a feed containing 67 percent hydrogen sulfide were predicted as follows.

2 Catalytic Stage Recovery	97.9 percent
3 Catalytic Stage Recovery	99.1 percent
4 Catalytic Stage Recovery	99.4 percent

The optimum yields for the lean-feed case (H_2S content of 10 to 50%) were predicted to be not significantly different. These efficiencies are based on the following practical factors.

(1) Furnace conversion cannot be predicted thermodynamically. In this example a value of 60 percent was chosen. This is lower than that which is generally observed.

(2) The gas off the first sulfur condenser was assumed to be 330°F.

(3) In consideration of certain side reactions, which must proceed in the first converter, an outlet temperature of 625°F was chosen. This temperature is well above the sulfur dew point.

The above predictions were tested in June, 1972 by the Western Research and Development Ltd. Calgary, Alberta on a Claus plant of 1600 MT/D capacity. Pertinent results of the field test are summarized in Table 11.

The agreement between actual and theoretical conversion and recovery tends to support the view that Claus plants can be operated at high enough conversion efficiencies to obviate the need for tail gas cleaning in most cases.

However, conversations with the Ralph M. Parsons Company, Los Angeles, California indicate that guaranteed efficiency of sulfur recovery cannot be made in excess of 97% (for new Claus plants). For old plants with efficiencies in the range of 90-97%, increasing the efficiency by any method will cost from 80 to 100 percent of the cost of a new Claus plant of equal capacity.

These discussions show the problems and potential solutions to improve H_2S conversion to sulfur in Claus plants. The other method of improving Claus plant efficiency is to use a tail gas unit. The variety of tail gas units available is described in a later section of this report.

Sulfur Recovery by Liquid-Phase Absorption-Oxidation Principle

Three processes using this principle are described in detail in

TABLE 11. SUMMARY OF CLAUS PLANT FIELD TESTS[2]

Stage	Feed	Conversion*		Recovery*		Operating Temperatures C		
		Actual	Theoretical	Actual	Theoretical	Condenser Outlet	Converter Outlet	Maximum Dew Point in Converter
Thermal Stage	98.31	66.6	-	-	-	190.6	-	-
Catalytic Stage #1	0.48	91.3	90.9	-	89.1	176.7	310	248.9
Catalytic Stage #2	0.43	97.5	97.3	-	95.9	165.6	215.6	207.2
Catalytic Stage #3	0.78	98.9	98.8	98.6	98.6	137.8	190.6	179.4
Catalytic Stage #4	-	99.3	99.3	99.1	99.1	123.9	171.1	148.9
Total	100.0	99.3	99.3	99.1	99.1	-	-	-

* Cumulative plant performance index in which all parameters are expressed as percentage of total plant feed.

Appendix C. These are the G-V sulfur process, the Stretford ADA vandate process, and the Takahax process. Although all these processes are in commercial operation as described in Appendix C, only the Stretford process appears to be important in the U.S. and will be discussed below.

The Stretford Process. The reactions upon which this process is based are essentially insensitive to pressure. Operating temperature throughout the unit are in the range of ambient to 49 C. A summary of the reactions is given below.

(1) Absorption of H_2S

$$H_2S + Na_2CO_3 \rightarrow NaHS + NaHCO_3 .$$

(2) Precipitation of sulfur

$$2NaVO_3 + NaHS + NaHCO_3 \rightarrow S\downarrow + Na_2V_2O_5 + Na_2CO_3 + H_2O .$$

(3) Regeneration of sodium vanadate

$$Na_2V_2O_5 + \text{ADA (oxidized)} \rightarrow 2NaVO_3 + \text{ADA (reduced)} .$$

(4) Regeneration of ADA

$$\text{ADA (reduced)} + \frac{1}{2}O_2 \text{ (air)} \rightarrow \text{ADA (oxidized)} .$$

(5) Overall reaction

$$H_2S + \frac{1}{2}O_2 \rightarrow S + H_2O .$$

COS and CS_2 are not recovered by the Stretford process and this reduces the overall sulfur recovery. Otherwise the Stretford solution is quantitative for the removal of H_2S. Some adverse side reactions occur due to peaks in loading (increased liquor temperature) and trace oxidizing gases contained in the fuel gas (notably oxygen, SO_2, and HCN) and result

in the buildup of sodium thiosulfate and related compounds in the circulating liquor which must be purged from the system. A typical analysis for the purge stream is shown in Table 12*. The rate of thiosulfate formation depends on the partial pressure of oxygen in the inlet gas stream, and the pH and temperature of the liquor. Formation of thiosulfate is quite low below about 38 C.

Disposal of Stretford Purge Solution. Currently, the Stretford purge stream normally is disposed of by discarding it to an industrial sewer. A process alternative that is being developed by Nittetu Chemical Engineering, Ltd. (NICE) involves treatment to reclaim the sodium value as Na_2CO_3 [12] (see Figure 4). As shown in the diagram, waste liquid removed from the desulfurization plant is first fed to the evaporator operated at 60 C and a vacuum of 100 mm. Hg (abs), where the salts are preconcentrated to about 50 weight percent. The evaporator heat source is quenched-combustion-gas obtained directly from the quenching tank at a temperature of about 90 C.

The concentrated waste liquid is then sprayed into the incinerator. Combustion of an auxiliary gas maintains the incinerator at 850 C in a reducing atmosphere. The reducing conditions are maintained by limiting the oxygen feed at 70-80 percent of the theoretical amount required for combustion. At the designated residence time, most of the sodium salts decompose to Na_2CO_3 and $NaHCO_3$; they are then blown into the quenching tank along with the hot combustion gas.

The quenching tank carries out two tasks: quenching of the hot combustion gas that is blown from the incinerator, and the capture of sodium salt contained in the gas, mainly Na_2CO_3. Quench and makeup water for the reconstituted Na_2CO_3 solution is fed through the gas-blowing duct between the incinerator and the quenching tank. The Na_2CO_3 solution is continuously removed from the tank and used as absorbent in the H_2S absorber.

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* Private communication from Charles Sedman, EPA, Durham, N.C. to Joseph Genco, BCL, Columbus (December, 1973).

TABLE 12. TYPICAL COMPOSITION OF STRETFORD PURGE SOLUTION[a]

Composition	Wt. Percent
Na_2CO_3	0.47
Na-ADS[b]	0.07
Na-Meta Vanadate	0.03
Na-Citrate	0.03
$Na_2S_2O_3$	0.60
NaSCN	0.60
H_2O	98.20

(a) Purge solution approximately 1.5 to 15 gal/100 moles of feed gas to the absorber.

(b) Na-anthraquinone disulfonate.

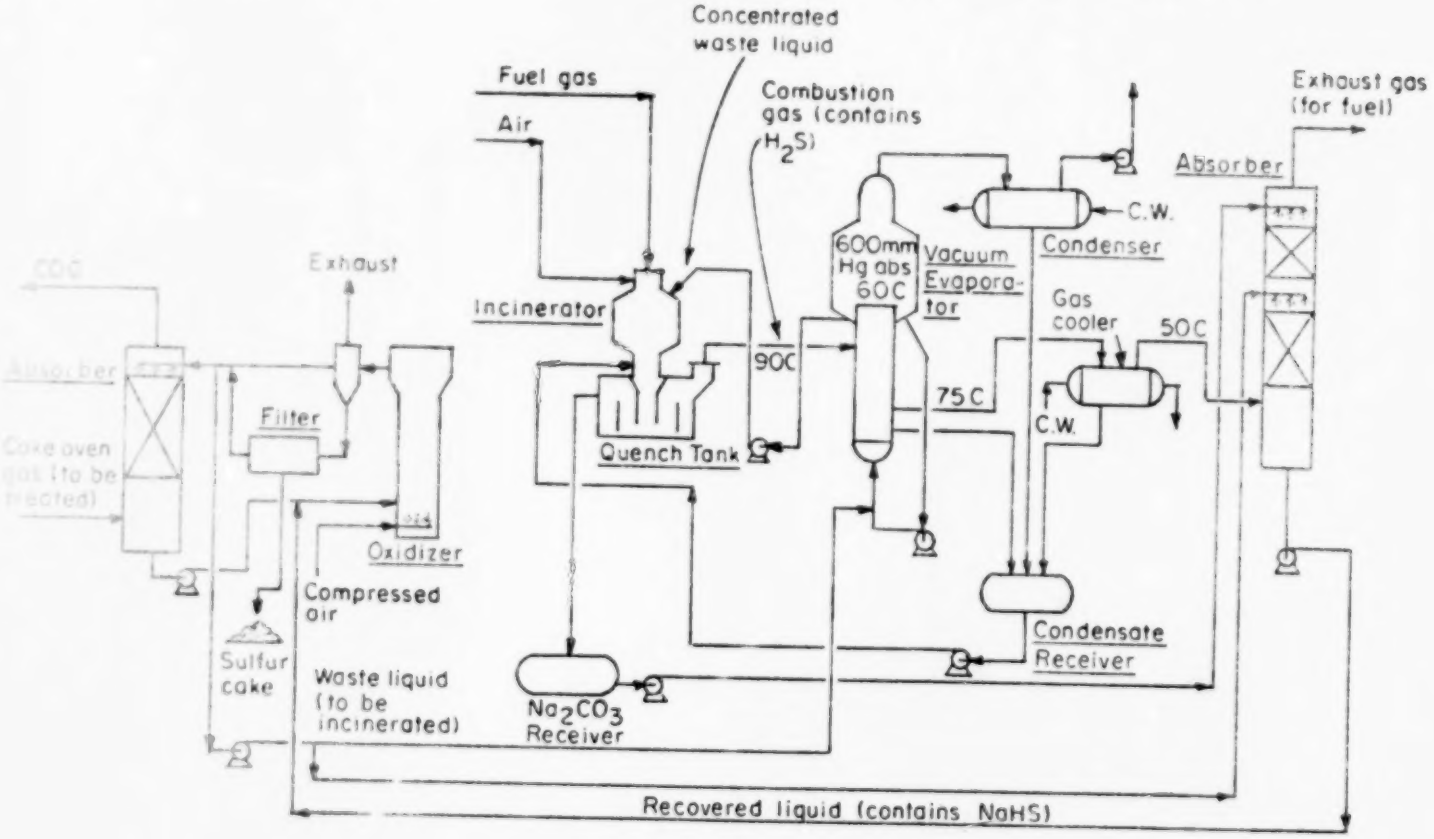

FIGURE 4. TREATMENT OF STRETFORD PROCESS PURGE SOLUTION[12]

The combustion gas, with sodium salts removed, is drawn out of the tank at approximately 90 C. This gas contains about 8 volume percent (dry basis) of H_2S as well as such gases as H_2, CO, and CH_4 and has a temperature of about 75 C when discharged from the shell side of the evaporator. It is cooled to about 50 C by a surface condenser and cooler before being supplied to the H_2S absorber.

The absorber is designed to return the absorbed H_2S that results from incineration under the reducing condition to the oxidizer at the desulfurization plant. There it is recovered from the filters as elemental sulfur. The Na_2CO_3 solution, recovered from the quenching tank, and the absorbent from the desulfurization plant are both recycled. Indication is that the NICE Process has been tried only at the pilot-plant level.

Tailgas Conditioning Processes

The six tail gas treatment processes in commercial use are listed in Table 13. Detailed process description and flow diagrams are presented in Appendix D.

Since tail gas processes are used to clean up the Claus plant effluent, the criteria of selection of any tail gas process are the same for both natural gas and refinery fuel gas applications. As is the case with any process selection problem, detailed design and economic evaluation of several alternate processes for a given gas stream will be necessary to arrive at the process giving optimum benefits.

TABLE 13. CLAUS PLANT TAIL-GAS TREATMENT PROCESSES

Process	Developer/Licensee	Commercial Units in Operation or Under Construction
Beavon	Union Oil, Ralph M. Parsons	7 in operation and 6 under construction
Cleanair	J. F. Pritchard, Texas Gulf Sulfur	1 in operation and 3 under construction
IFP-1	Institut Francais du Petrole	12 in operation and 5 under construction
SCOT	Shell Development	2 in operation and 25 under construction
Sulfreen	Lurgi, SNPA*, Ralph M. Parsons	3 in operation and 4 under construction
Wellman-Lord	Davy Powergas	2 in operation and 6 under construction

* Societe Nationale des Petrole d'Aquitaine.

VI. ASSESSMENT OF SULFUR RECOVERY IN NATURAL GAS PROCESSING

Natural gas and liquid processing plants reporting sulfur recovery for 1972 are listed in Table 14[1,6]. Accordingly 24 states in the U.S. processed natural gas; however, sulfur recovery from sour gas was done in only seven of these states, namely, Arkansas, Florida, Mississippi, New Mexico, North Dakota, Texas, and Wyoming. The total sulfur recovery amounted to 2443 MT/D (metric tons/day also equal to kkg/day) and the associated gas throughput volume was 33 MMscumd (1162 Million scfd). Thus the average H_2S concentration in the gas processed for sulfur recovery is computed to be about 5.5 volume percent or 35 grains per scf. A salient summary by state is also presented in Table 15.

The following points of significance are noted from Tables 14 and 15.

(1) Total sour gas (33 MMscumd) is only about two percent of the total daily gas production rate of 1608 MMscumd (56787 MMscfd).

(2) Nearly 100% of the gas produced in 17 states including Louisiana, California, Kansas, Oklahoma is sweet.

(3) The total sulfur produced by the gas processing industry is about one million tons per year. If the Claus plants used in this production is assumed to be 95 percent efficient, the emissions from the industry would be 50,000 tons of sulfur per year in 1972. Comparison of this emission with the total SO_2 emissions for the nation as a whole represented by the Council on Environmental Quality[7] (CEQ) is made in Table 16. Accordingly SO_2 emission from natural gas processing is 0.30% of the total national SO_2 emissions during 1972-1973.

TABLE 14. NATURAL GAS AND LIQUID PROCESSING PLANTS[1,6] REPORTING SULFUR RECOVERY (1973)

State	Company and Plant	Sour-Gas Production (MMscumd)	Sulfur Production (MTD)
Arkansas	Arkansas Louisiana Gas Company		
	Hamilton Plant, Various Fields, Columbia	0.9	5.3
Florida	Exxon and other companies		
	Jay Field Facilities, Santa Rosa and Escambia Counties	3.7	650
Mississippi	Shell Oil Company - Goldwater Plant and Field, Clarke County	0.17	1.4
	Thomasville Plant and Field, Rankin County, Jackson	0.40	220
New Mexico	Amoco, Empire Abo Plant and Field, Eddy County	0.68	22
	Cities Services Oil Company, Bluitt Plant, Chaveroo, Roosevelt County	0.85	8
North Dakota	Signal Oil and Gas Company, Tioga Plant, Williams County	2.12	116
Texas	Amoco, Edgewood Plant and Field, Van Zandt County	0.86	332
	Midlands Farm Plant, Andrews County	1.00	6
	North Cowden Plant, Ector County	2.6	26
	Slaughter Plant & Field, Mockley County		34
	South Fullerton Plant, Andrews County	0.82	3
	West Yantis Plant. Wood County	0.51	34
	City Services Oil Company, Lehman Plant, Cochran County	0.37	2
	City Services Oil Company, Myrtle Springs Plant, Van Zandt County	0.76	216
	Robstown Plant, Nueces County		
	Simon X Perry's Subdivision of Fred Tract	0.59	216
	Seminole Sulfur Plant, Seminole County	0.79	23
	Welch Plant, Dawson County	0.05	2
	Exxon Company, Jourdonton Plant, Atascosa County	0.62	13.2
	Gulf Energy and Development Corporation, Powell Plant, Navarro County	0.30	6
	Odessa Natural Corporation, Foster Plant, Ector County	0.54	12.8

TABLE 14. (Continued)

State	Company and Plant	Sour-Gas Production (MMscumd)	Sulfur Production (MTD)
Texas	Shell Oil Company, Bryan's Mill Plant, Cass County	1.56	190
	Shell Oil Company, Person Plant, Karnes County	1.41	20
	Warren Petroleum Company, Como Plant, Hopkins County	0.34	34.6
	Warren Petroleum Company, Fashing Plant, Atascosa County	1.40	27.4
	Warren Petroleum Company, Sand Hills Plant, Crane County	4.1	33.4
	Warren Petroleum Company, Waddel Plant, Crane County	3.4	89.2
Wyoming	Amoco Production Company, Beaver Creek Plant, Fremont County	1.47	39
	Amoco Production Company, Elk Basin Plant, Park County	0.31	32
	Husky Oil Company, Ralston Plant, Park County	0.15	29
TOTAL		33.0	2,443.3

TABLE 15. SALIENT DATA ON SULFUR RECOVERY IN NATURAL GAS PROCESSING

State	Total Sulfur Production (MT/D)	Associated (Sour) Gas Throughput (MMScfd)
Arkansas	5.3	31.9
Florida	650	130
Mississippi	221.4	20
New Mexico	30	54.3
N. Dakota	116	74.8
Texas	1,320.6	783.0
Wyoming	100	68.2
Total	2,443.3	1,162.2

TABLE 16. COMPARISON OF SO_2 EMISSIONS FROM ALL SOURCES

	MT/Y	SO_2 From Natural Gas As Weight Percent of SO_2 From Other Sources
Natural gas industry CEQ Data[7]	0.10[a]	-
All industrial processes	5.1	2.35%
Stationary sources using fuel combustion	26.3	0.46%
Transportation	1.0	12.0%
Solid Waste Disposal	0.1	120.0%
Miscellaneous	0.1	120.0%
Total (except SO_2 from natural gas	32.6	0.30%

(a) Based on an average sulfur recovery of 95 percent in existing Claus plants and on a total sulfur production from natural gas industry of about one million tons per year (MT/Y). Texas and Louisiana state laws require Claus plants to achieve and maintain a minimum of 94 to 97 percent sulfur recovery depending on the size of the plant.

Listing of Sour Gas Processes in Texas

Attempts were made to obtain accurate data on the extent of unrecovered H_2S emission from oil and gas processing plants in Texas. Such information was theoretically available in the files of the Railroad Commission of Texas*. Accordingly, this agency was contacted and information on H_2S emissions and sulfur production for 77 plants (GP-1 forms) in Texas was obtained. However, upon carefully checking the forms, it was found that the information available did not differentiate between the acid gas and H_2S even though very often the acid gas contained 90 percent CO_2. As a result, the data available in GP-1 forms were suspect. For other states, no such data are available.

In summary, a state wide - plant wise emission inventory for H_2S requires a major effort. However, the objectives of this report do not suffer due to the lack of such data because it has already been shown that (1) small operators comprise only about 2 percent of the total gas processing capacity, (2) the sour gas production is less than 5 percent of the total gas produced in the U.S., and (3) a sufficiently accurate data on Claus plants producing sulfur for every state is available from which an estimate of sulfur emissions can be made.

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* See listing for Mr. James C. Bouldin in Appendix F. All plants processing gas report to the Railroad Commission of Texas on Form GP-1 entitled "Monthly Report for Gas Processing Plants".

VII. OVERALL ASSESSMENT AND RECOMMENDED CONTROL OPTIONS

The US natural gas processing industry operates about 800 processing installations of three different size ranges described in Table 17. The combined processing capacity of these installations was 1.6 billion/scumd as of January, 1973. Of this gas volume, 33 million cumd was sour gas. Thus, sour gas represents about two percent of the total gas volume. It is quite possible that many small gas plants processing less than 0.3 million cumd of sour gas with low H_2S (100 ppm) concentration are not represented in this sour gas volume of 33 cumd. But such unreported volume is not expected to be more than about a few million/scumd, as a reasonable guess.

As reported in Section II, the H_2S concentration in the sour gas ranges from 100 to 106,000 ppm (0.25 to 270/gm/scum) although isolated fields have produced natural gas with up to 600,000 ppm of H_2S. However H_2S levels in processed sour gas which led to the production of sulfur in 29 reported plants[1] averaged 74 gm/scum. Of these 29 plants, four were small sized, 16 were in the intermediate size rnage and 9 in the large size range of processing facilities. This fact and other useful analytical conclusions are summarized in Table 17.

Also presented in Table 17 is the effect of H_2S recovery efficiencies obtainable with Claus plant and other processes on sulfur emission levels for the three size ranges.

Effect of Claus Plant Efficiency on SO_2 Emissions

The following conclusions can be drawn from the data in Appendix I and Table 17.

(1) Small gas plants contribute 1.6 percent of the total SO_2 emission from all the gas plants at the three sulfur recovery levels of 95%, 97% and 99.5 percent.

(2) In absolute quantities, the reduction in SO_2 emission from small plants realized by increasing the sulfur recovery efficiency from 95 percent to 99.5% will be 85,000 MT/Y and is not significant in comparison with about 33 million MT/Y of SO_2 emission for the nation as a whole.

TABLE 17. ANALYSIS OF REPORTED DATA[1] (1973) ON NATURAL GAS PROCESSING PLANTS REPORTING SULFUR PRODUCTION

Item	Classification of Natural Gas Processing Facility by Size			
	Small	Intermediate	Large	Total
Size range MMscumd	<0.3	0.31-1.13	1.14-52.7	-
No. of plants[1] (1972)	4	16	9	29
Volume of sour gas				
Processed MMscumd	0.67	10.34	21.99	33.00
Sulfur produced MT/D (1972)	38.4	1179.9	1225.0	2443.3
%	1.6	48.3	50.1	100.0
Average H_2S in raw gas				
ppm	40042	79720	41,000	-
gm/scum	57.31	114.10	58.70	-
grains/100scf	2502	4982	2561	-
Effect of sulfur recovery efficiency				
(1) SO_2 emission at 95%[b] recovery MT/D	4.0[a]	124.2[a]	129.0[a]	257.2
10^6MT/Y	0.0015	0.0450	0.0470	0.0939
%	1.6	48.3	50.1	100.0
(2) SO_2 emission at 97%[c] recovery MT/D	2.4	73.0	175.8	151.2
10^6MT/Y	0.0009	0.0270	0.0280	0.0550
%	1.6	48.3	50.1	100.0
(3) SO_2 emission at 99.5%[d] recovery MT/D	0.386	11.86	12.31	24.55
10^6MT/Y	0.0001	0.0043	0.0045	0.0090
%	1.6	48.3	50.1	100.0

(a) SO_2 = 2 (sulfur produced) (100-e)/e where e = Claus plant efficiency in %.

(b) Average existing Claus plant efficiency is about 95%.

(c) Probably attainable by increasing the Stages to 3 and in some cases 4 in Claus plants.

(d) Will require tail-gas cleaning to attain 99.5% efficiency.

(3) Intermediate and large plants produce about the same quantity of sulfur and benefits of increasing the sulfur recovery from these sizes are about the same.

(4) If the current average Claus plant efficiency is assumed to be 95%, the natural gas industry at current sulfur production levels contributes about 0.1 million MT/Y of SO_2 to the national SO_2 emission of about 33 MT/Y. Thus, about 0.3% of the national SO_2 emissions are due to the Claus plants in natural gas.

(5) If the efficiency of all Claus plants is raised to 97%, the SO_2 emissions would be reduced from 0.1 to 0.055 million MT/Y, i.e., to 0.17 percent of the total national SO_2 emissions. However, if the actual Claus plant sulfur production reaches the full production capacity indicated in Appendix I, for the 84 plants, the SO_2 emission at 97% Claus plant efficiency will be 386 MT/D* which is about 0.43% of the national SO_2 emission level of 33 million MT/Y.

(6) If each of the 84 Claus plants were allowed to emit 2 tons of sulfur per day, the total emission of SO_2 would be 0.123 million MT/Y. This represents 0.37 percent of the total annual national SO_2 emission.

Control Options and Performance Standards

The various control options available to reduce the emission of H_2S and/or SO_2 in the natural gas industry depend on the degree of emission reduction specified for each facility size. The required degree of emission reduction is derived from the allowable sulfur emission that would not significantly contribute to the national SO_2 emissions. These factors

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* 386 MT/D = (2) x (6249) (100-97)/97 since one ton of sulfur (S) produces two tons of sulfur dioxide (SO_2).

determine the needed performance standards for sulfur recovery units in natural-gas processing.

The control options possible for three hypothetical levels of allowable emissions are shown in Tables 18 through 20. In all of the hypothetical, allowable levels* A, B, and C, seven control categories result. The various control options suggested are:

(1) Reinjection of acid gas
(2) Iron oxide process
(3) Molecular sieve process
(4) Packaged Claus plant
(5) 2- and 3- and 4-stage Claus plant
(6) Tail-gas units with Claus plant.

Each of these options is briefly discussed below.

(A) Reinjection of Acid Gas or Separated Sour-Gas to Well Formations

Reinjection is possible and economically feasible when it assists a production field in secondary gas/oil production and when the wells in the field are unitized. The decision to reinject is up to the gas processors. There is one facility practicing reinjection in Alberta[13]. Some of the problems of handling H_2S under high pressure are listed in Appendix H. A brief summary of the reinjection problems is listed below.

The most serious problems to be encountered in reinjection of the separated sour gas or of the treating plant regenerator off gases are:

(1) Dehydration of gas prior to handling in injection service.
(2) Hazards associated with handling high-pressure toxic material like H_2S and CO_2.
(3) Costs associated with the designing and installation of a safe, noncorrosive system, in unitizing the mineral rights of the receiving subsurface formation, and protecting the producing wells bottomhole equipment which would be exposed to the high concentration of acid gases in the producing reservoir after reinjection.

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* Defined in Tables 18, 19, and 20.

TABLE 18. CONTROL OPTIONS AT HYPOTHETICAL ALLOWABLE EMISSION LEVEL "A"

Control Category Number	Gas Plant Size as Sweet Gas Production Rate MMscumd	Gas Plant Size as Sweet Gas Production Rate MMscfd	Sulfur Production Rate MT/D	Allowable Sulfur Emission MT/D	Required Sulfur Recovery Efficiency %	Control Options
1	Any	Any	≤1.0	1.0	0	Tall Stack dispersion when ground level concentration of H_2S/SO_2 is high
2	≤0.3	<10.5	>1 to ≤10	1.0	0% at 1 MT/D 90% at 10 MT/D	(1) Reinjection of gas (2) Iron oxide process (3) Molecular Sieve Process (4) Packaged Claus plant
3	≤0.3	<10.5	>10	-	94%	(1) 2 or 3 stage Claus plant
4	>0.3 but ≤1.13	>10.5 but ≤40	>10 but ≤40	1.0	90% at 10 MT/D 97.5% at 40 MT/D*	Low efficiency Claus plant High efficiency (4 stage) Claus plant
5	>0.3 but ≤1.13	>10.5 but ≤40	>40	-	97.5%*	High efficiency (4 stage) Claus plant
6	>1.13	>40	40 to 500	1.0	97.56% @ 41 MT/D* 99.00% @ 100 MT/D 99.50% @ 200 MT/D 99.7% @ 500 MT/D	High efficiency Claus plant Tail gas + Claus plant Tail gas + Claus plant Tail gas + Claus plant
7	>1.13	>40	>500		99.8%	Tail gas + Claus plant

* Current indications are that obtaining a Claus plant sulfur recovery efficiency of >97.5 percent would require tail gas cleaning systems. The cost of such systems range from 80 to 100 percent of the cost of the Claus plant.

TABLE 19. CONTROL OPTIONS AT HYPOTHETICAL ALLOWABLE EMISSION LEVEL "B"

Control Category Number	Gas Plant Size as Sweet Gas Production Rate		Sulfur Production Rate, MT/D	Allowable Sulfur Emission, MT/D	Required Sulfur Recovery Efficiency, percent	Control Options
	MMscumd	MMscfd				
1	Any	Any	≤2.0	2.0	0	Tall stack dispersion when ground level concentration of H_2S/SO_2 is high
2	≤0.3	<10.5	>2 to ≤10	2.0	0% at 2 MT/D 80% at 10 MT/D	(1) Reinjection of acid gas (2) Iron oxide process (3) Molecular sieve process (4) Packaged Claus plant
3	≤0.3	<10.5	>10	---	≥80%	Packaged Claus plant
4	>0.3 but ≤1.13	>10.5 but ≤40	>10, ≤40	2.0	80% at 10 MT/D	Packaged Claus plant
					95% at 40 MT/D	2-stage Claus plant
5	>0.3 but ≤1.13	>10.5 but ≤40	>40	---	≥95%	3-stage Claus plant
6	>1.13	>40	40 to 500	2.0	95% at 40 MT/D 98% at 100 MT/D 99% at 200 MT/D 99.6% at 500 MT/D	2-stage Claus plant Claus plant + tail gas Claus plant + tail gas cleanup Claus plant + tail gas cleanup
7	>1.13	>40	>500		≥99.6%	Claus plant + tail gas cleanup

TABLE 20. CONTROL OPTIONS AT HYPOTHETICAL ALLOWABLE EMISSION LEVEL "C"

Control Category Number	Gas Plant Size as Sweet Gas Production Rate MMscumd	MMscfd	Sulfur Production Rate, MT/D	Allowable Sulfur Emission, MT/D	Required Sulfur Recovery Efficiency, percent	Control Options
1	Any	Any	≤2.0	2.0	0	Tall stack dispersion when ground level concentration of H_2S/SO_2 is high
2	<0.3	<10.5	>2, ≤10	2.0	0% at 2 MT/D 80% at 10 MT/D	(1) Reinjection of acid gas (2) Iron oxide process (3) Molecular sieve process (4) Package Claus plant
3	<0.3	<10.5	>10		90%	
4	>0.3 but ≤1.13	>10.5 but ≤40	>10, ≤20	1.0	90% at 10 MT/D	2-stage Claus plant
					95% at 20 MT/D	2-stage Claus plant
5	>0.3 but ≤1.13	>10.5 but ≤40	>20		95%	3-stage Claus plant
6	>1.13	>40	20-500	2	95% at 20 MT/D	2-stage Claus plant
				3	97% at 100 MT/D	4-stage Claus plant
				4	98% at 200 MT/D	Claus plant + tail gas cleanup*
				5	99% at 500 MT/D	Claus plant + tail gas cleanup*
7	>1.13	>40	>500		≥99%	Claus plant + tail gas cleanup

* The 98% to 99% efficiency may be attainable with the IFP-1 tail-gas cleanup process which appears to have a much lower overall energy and capital requirement.

(4) The cost of installing adequately rated equipment in high-pressure service. This cost depends on the geometry of the system as well as the injection pressures required and the volumes of gases to be handled. These costs may be so high that an operator, simply because of economics (cost versus benefit), cannot afford to make the necessary investment in dehydration equipment, compressors, high-pressure lines and fittings, well conversion cost, etc., and may elect to prematurely abandon his production which is responsible for the generation of the sour gas.

(5) Proper consideration must be given the effect of treating plant regenerator off gas injected on the resultant concentration of sour gas components in the receiving formation and its effect on the wellbore equipment in close proximity to the injection well.

(6) Underground reinjection of sour or acid gases as well as any other extraneous fluid will, in most cases, require complete unitization of all the mineral interests involved in the project to protect correlative rights of all the interests involved. Depending upon the complexity of ownership, this unitization effort could take years to conclude. This time delay and effort could add to the cost of the project and may also, in itself, make the project uneconomical.

(B) Use of Iron Oxide Process

This process removes H_2S from the natural-gas stream to almost zero level. Thus, in a small facility, a portion of the gas can be sweetened and mixed with the remaining sour gas so that the total H_2S in the natural-gas mixture does not exceed pipeline or other specifications. The small operator may be able to reduce his H_2S emission to less than one MT/D by using the iron oxide process because the process produces solid waste but no H_2S emissions. Burning the spent sponge would, of course, result in emitting SO_2 equivalent to the amount of H_2S removed from the gas.

(C) Use of the Molecular Sieve Process

This is an alternative to the iron sponge process insofar as it can be quite selective in removing H_2S (and other sulfur compounds) but not CO_2, and the comments made above apply to this process also. However, regeneration of the sieve, unless the non-commercial Haines arrangement is utilized results in the release of the adsorbed H_2S which must then be disposed of.

(D) Packaged Claus Plant

When a maximum of only about 90 percent H_2S conversion to sulfur is required, a packaged two-stage Claus plant may provide a suitable option at low cost. The cost of the packaged Claus plant in relation to cost of the facility and other available options, if any, needs to be evaluated.

(E) Tail-Gas Cleanup with Claus Plant

There are at least six commercially used tail-gas cleaning processes with many more under various stages of development. The six processes, details of which are presented in Appendix C, are

(1) Beavon Process
(2) Cleanair Process
(3) IFP Process
(4) SCOT (Shell Claus Offgas Treating) Process
(5) Sulfreen Process
(6) Wellman-Lord (W-L) SO_2 Recovery.

There are advantages and disadvantages associated with the employment of any of these processes for a particular application. All of the processes require electrical energy; the amount of energy used usually increases in proportion to the desired degree of sulfur removal for the tail gas. It could be useful to compare the increased emission of SO_2 at the coal-fired power plant resulting from the increased use of electric power at the natural-gas plant necessitated by the tail-gas units. Both are point sources and both require energy for SO_2 emission control. Some aspects of

the operational data of these tail-gas cleaning processes are discussed in Section VIII.

One other control option not related to the emission of sulfur from acid gas is the use of vapor recovery units on oil storage tanks employed in LACT systems described earlier. The Texas Air Control Board informs that all new storage tank installations do include vapor recovery units which compress the small amount of vapor leaking from the tanks and inject the compressed vapor to sales or plant inlet gas lines. The injection of a small amount of H_2S by this method into sales gas lines would be permissible only if the resultant mixture does not exceed the allowable H_2S level of the gas. This practice appears to be a sound and reasonable approach to the prevention of small-volume H_2S emission at remotely located LACT units.

VIII. OPERATIONAL DATA FOR SELECTED PROCESSES

The study of the natural-gas processing systems described in the preceding Sections of this report indicates that control options which may be used in reducing the SO_2 emissions from the industry as a whole are as follows:

(1) Reinjection of the sour-gas and acid gas to well formation
(2) Iron oxide process for H_2S removal
(3) Molecular sieve process for H_2S removal from sour gas
(4) Packaged Claus plant
(5) 2- and 3-stage Claus plant
(6) 4-stage Claus plant
(7) Claus plant with tail-gas unit
(8) Tail-gas cleaning units (TCU's)
    (a) Beavon
    (b) Cleanair
    (c) IFP-1 and IFP-2
    (d) SCOT
    (e) Sulfreen
    (f) W-L SO_2 recovery

For the six TCU's listed, detailed operational and process description data are presented in Appendix D. However, a convenient overall summary of the data is also presented in Table 21. It can be seen that the IFP-1 process which can increase the Claus plant sulfur recovery to about 98.5%, has the lowest utility consumption and perhaps the lowest total capital requirement. The waste stream from this process consists of intermittent (once every two years) waste waters generated in catalyst washing. The process off-gas leaving the top of the ammonia scrubber containing traces of NH_3, entrained polyalkylene glycol solution, and occasionally fine white particulate fume is another minor waste stream. A study is currently in progress to determine the least expensive method to eliminate the particulate fume[11]. Both these waste streams can be considered to constitute a minor environmental problem.

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TABLE 21. OPERATIONAL DATA FOR TAIL GAS CLEANING PROCESSES

Process Name	Operating Features	Product From Process	Sulfur in Exit Gas	Costs as of April, 1973*			Secondary Waste Streams**
				Investment	Utilities	Operating	
Beavon	Reduction of tail gas constituents to H_2S followed by sulfur recovery with Stretford unit	99 percent pure Sulfur as molten or cake. Particle size 0.3 to 25 microns	<100 ppm Total S <10 ppm H_2S	For a 100 MT/D Claus unit, $700,000 to $1 million	Steam - 1,453 Kg/hr Cooling water - 1/sec Electricity - 25 kwh/hr Fuel gas - 224 scmh	-- Maintenance 2 percent of capital 1/2 man/shift	Stretford purge solution (see text, page 53) and sour water condensate
Cleanair	Recovers 99.9 percent of sulfur from Claus plant tail gas	99.5 to 99.9 pure sulfur	<200 ppm by volume	$500,000 for a 10 MT/D Claus plant $3,000,000 for a 1000 MT/D Claus plant	For a ton of sulfur produced in Claus plant per day Steam - 22 Kg Electricity - 4 kwh Cooling water - 34 l/hr	--	Purge waste water stream
IFP-1 (TGT-1500)	Designed for low cost and sulfur recovery efficiency of about 98.5 percent	Bright yellow sulfur 99.9 percent pure	~2000 ppm of SO_2	$2 million for a 1400 MT/D Claus plant with 96.5 percent efficiency and 99 percent overall sulfur recovery $450,000 for 200 MT/D Claus plant	Steam: for start up only Electricity - 35 kwh/hr Cooling water - for shut down only Fuel gas - 0	$30/day $347/day for catalyst and solvent	Intermittent water contaminated with alkali metal salts and organic acid
IFP-2 (TGT-150)	High sulfur recovery (99 percent plus) at a cost higher than IFP-1	Bright yellow sulfur 99.9 pure	~500 ppm of SO_2	$800,000 for 250 MT/D Claus plant at 95 percent efficiency	$70/day	Catalyst plus solvent, $5/day	NH_3 - SO_2 fume plus waste water stream as in TGT-1500
SCOT	Increases sulfur recovery of Claus plant from 95 percent to 99.8 percent by reduction and alkanolamine absorption. Can handle varying feed rate and composition	Pure and bright yellow sulfur	<300 ppm of SO_2	70 to 100 percent of the cost of Claus plant	For a 250 MT/D Claus plant at 94 percent efficiency Boiler water - 2500 Kg/hr LP steam - 2,910 Kg/hr Fuel gas - 100 Kg/hr Reducing gas - 26 Kg/hr Electricity - 350 Kw	Maintenance 2 percent of capital	Substantially none A very small amount of degrade solvent is generated
Sulfreen	Essentially an extension of the Claus process after CS_2 in tail gas is reduced to H_2S. Sulfur yield to about 99 percent	Liquid sulfur, 99.9 percent pure, bright yellow	~1000 ppm of SO_2	For a 1000 MT/D Claus plant, $2 million	Electricity - 650 kwh Boiler water - 40 l/min Fuel gas - 9900 scmd	--	No liquid wastes Catalyst life - 4 years Solid waste is generated as used alumina catalyst
Wellman-Lord SO_2 recovery	Treats only SO_2 (hence tail gas incineration is a must)	Concentrated SO_2	<100 ppm of SO_2	For a 200 MT/D Claus unit, $1.6 million	Cooling water - 500** Kg/hr Electricity 220 Kw NaOH - 1 MT/D	--	Purge stream containing metal salt are sent currently to industrial sewers

* To update these costs to April, 1974, multiply April, 1973 costs by an approximate CE plant cost index ratio of 1.1.

** For quantitative data see Reference (11), a recent report from BCL to OAQPS, EPA, Durham, North Carolina.

Data for Claus Plants

The most significant waste stream from a Claus plant is the tail gas which contains sulfur equivalent to 3 to 5 percent of the feed sulfur concentration. This aspect has been discussed in detail in earlier Sections of this report.

The second significant waste stream is the spent catalyst (usually bauxite) generated from the Claus catalytic reactors. The amount of spent catalyst is a function of the number of catalytic conversion stages employed, which, in turn, is a function of the required sulfur recovery efficiency. Thus, to maintain an efficiency greater than 97 percent, the catalyst may have to be replaced every 12 to 18 months. Currently, most plants replace the catalyst between the third and fourth years and efficiencies obtained range from 94 to 97 percent. One plant reports that about 20 MT of spent catalyst is usually generated once in 3 to 4 years from a 200 MT/D Claus plant. The spent catalyst is not regenerated and hence constitutes a solid waste burden. The quantity of solid wastes generated is relatively insignificant and toxic or leachable substances are not expected to be present. For these reasons, it should be possible to dispose of the spent catalyst in a landfill. However, it should be pointed out that no analyses of the spent catalyst are available to make a definite determination of its toxicity.

IX. REFERENCES

(1) Cantrell, Ailleen, "1973 Survey of Gas Processing Plants", Oil and Gas Journal (July 9, 1973).

(2) Rankine, Robin. P., Kerry, R. K., et al "Potential Efficiencies of the Conventional Claus Sulfur Recovery Process", a paper presented to the Alberta Sulfur Gas Research Workshop, Edmonton, Alberta, Canada, November 1, 1973, by Western Research and Development Ltd., Calgary, Alberta, Canada.

(3) Chalmers, W. W., et al "Improvements to the Claus Process--Past, Present and Future" Paper No. 71-AP-8. Presented at the 1971 Annual Meeting of APCA, Pacific NW International Section, Calgary, Alberta, Canada (Nov 21-23, 1971).

(4) Horner, W. N., "Operating Parameters at Ram River Plant Outlined", Gas Processing, Canada, (March-April, 1973), Page 14.

(5) Reprint from the 1972 "Bureau of Mines Mineral Year Book" - Natural Gas Section, U.S. Department of Interior, Washington, D.C.

(6) Telephone Conversation with Mr. John Flynn, Chief Gas Processing Engineer, Shell Oil Company, Houston, Texas (Phone 713/220-5440) and with Mr. Carl T. Hester, Exxon Production Company, U.S.A., Houston, Texas (Phone 713/221-3563).

(7) "Environmental Quality" - The Fourth Annual Report of the Council on Environmental Quality, September, 1973. Page 266, Published by U.S. Government Printing Office, Washington, D.C. 20402.

(8) Encyclopedia of Chemical Technology, Edition 2, 10, Pages 390-420. (1965) Kirk and Othmer Interscience Publishers, Division of John Wiley, New York, N.Y.

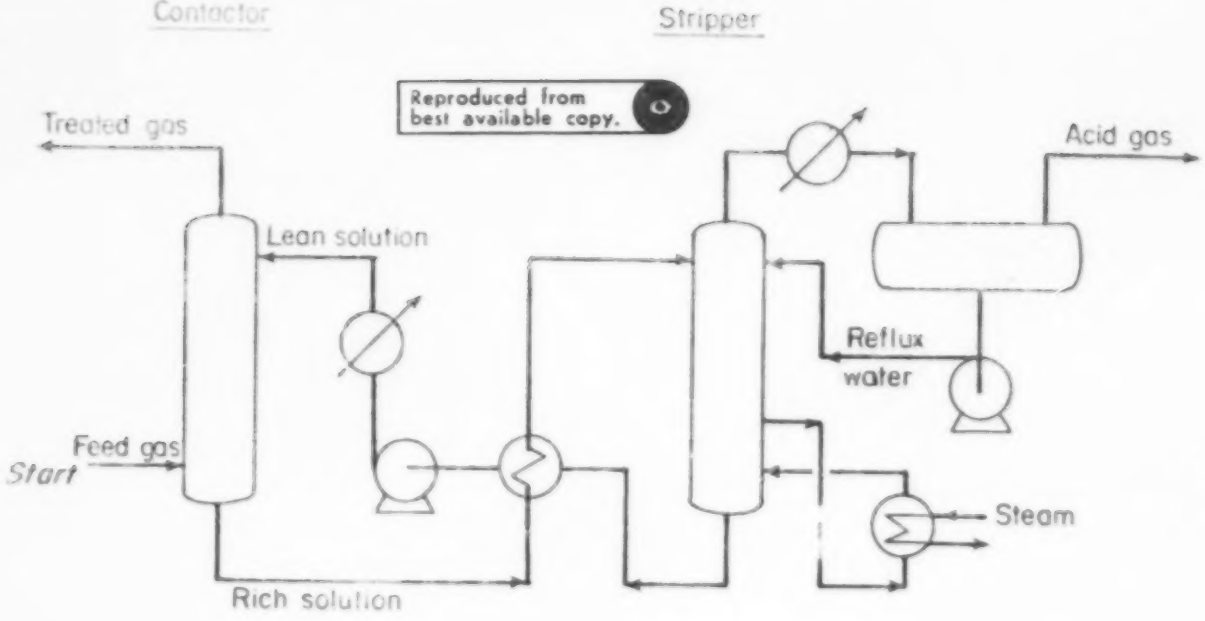
(9) Beers, W. D., "Characterization of Claus Plant Emissions", EPA Report No. EPA-RD-73-188 (NTIS PB 220-376) from Process Research Inc., Cincinnati, Ohio. (April, 1973).

(10) Maddox, R. N., Gas and Liquid Sweetening, 2nd Edition, John M. Campbell Company, Norman, Oklahoma (1974).

(11) Gomez, J. M., and Tan, S. S., "Final Report on Characterization of Sulfur from Refinery Fuel Gas" Report to EPA, Durham, N.C., under Contract No. 68-02-0611 (June 28, 1974).

(12) Hitachi, K., Chemical Engineering, 80 (21), 78-79 (October 15, 1973).

(13) Haraniuk, E.M., "Sour Gas Compression at the West White Court Plant" Journal of Canadian Petroleum Technology, January-March, 1968.



Fluor Econamine

Application: For the removal of acidic impurities, H_2S and CO_2, from gas streams. The treating agent used is an aqueous solution of the primary alkanolamine, $HO\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}NH_2$, tradenamed Diglycolamine (DGA).

Product: Natural, synthesis or refinery gas streams may be treated to H_2S levels of less than 0.25 grains/100 scf and to CO_2 levels less than normally attained with conventional MEA or DEA treating.

Description: The process scheme is identical to any other alkanolamine treating plant. In fact, several existing MEA treating plants have been switched to Fluor Econamine with no equipment changes.

Feed gas is purified in a contactor vessel where acidic impurities are absorbed by the Fluor Econamine solution. Treated gas flows to dehydration or other subsequent processing. Rich solution is heated by interchange with hot lean solution, then flows to the stripper vessel for solution regeneration. Stripped acid gases and water vapor pass overhead to the condenser. Condensed water is refluxed to the stripper while H_2S and CO_2 go to flare or to sulfur recovery. Stripping heat is furnished by a steam-heated reboiler. Lean solution circulates from the stripper, through the exchangers, and is pumped through solution coolers to the top of the contactor.

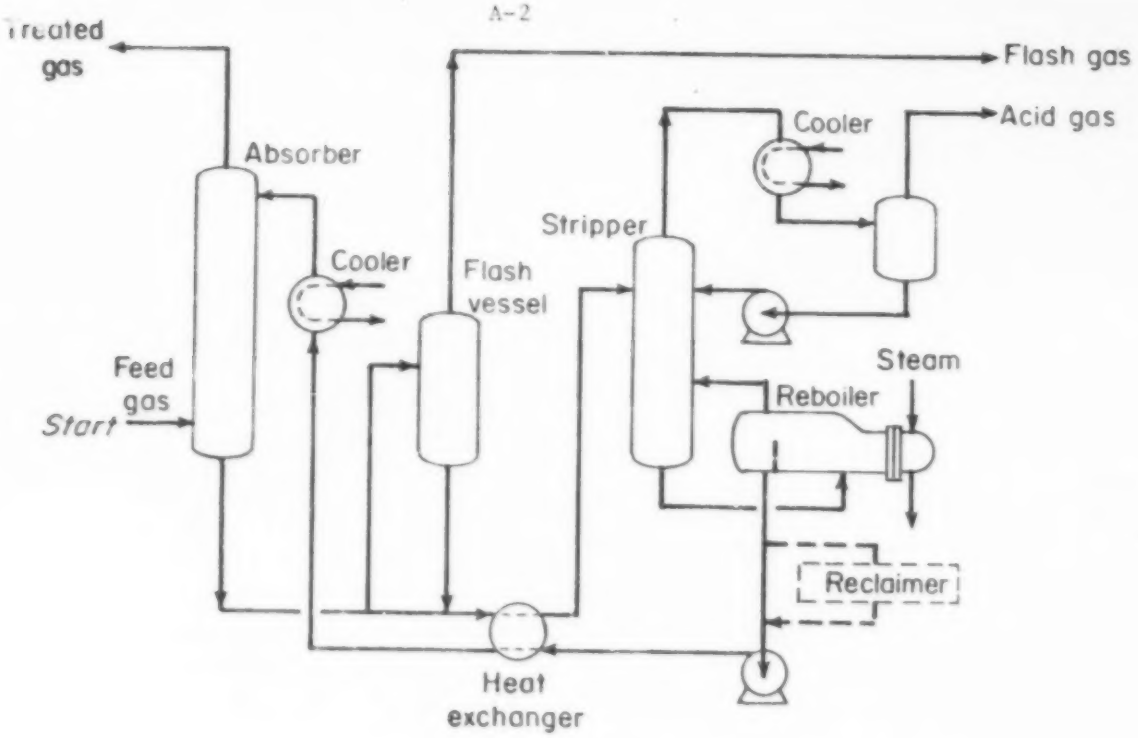
The solution is typically 65 percent by weight DGA or higher. Use of this high concentration permits reducing circulation rate by, typically, 25-40 percent compared to MEA treating. This results in substantial savings in both capital and operating costs. At the same time, experience has demonstrated that corrosion is comparable to or less than normally experienced with conventional amines.

Degradation of the treating solution is prevented by the use of a simple and inexpensive high temperature reclaiming technique, which purifies a slipstream of the treating solution. No caustic or other chemical addition is involved in this operation. Solution makeup requirements are generally below those of conventional amine processes. This reclaiming method permits the use of the Econamine Process for gas streams containing COS or CS_2 since the decomposition products formed by the reaction between these sulfur impurities and the DGA are also thermally regenerated during the normal reclaiming operation.

Commercial Installations: Econamine is in use in 19 plants with an aggregate capacity of well over 1 billion standard cubic feet per day.

Reference: *Oil and Gas Journal*, May 2, 1966, pp. 83-86.

Licensor: Fluor Engineers and Contructors, Inc.



Sulfinol

Application: Process removes acidic gas constituents such as H_2S, CO_2, COS, mercaptans, etc., from natural, refinery and synthesis gases, and LNG feedstocks.

Description: The process is based on the use of an organic solvent, Sulfolane (tetrahydrothiophene dioxide) mixed with an alkanolamine, and water. Simultaneous physical and chemical absorption under feed gas conditions is provided by this Sulfinol solvent, and regeneration is accomplished by release of the acidic constituents at slightly above atmospheric pressure and at elevated temperature.

Feed gas is contacted with regenerated Sulfinol solvent in the absorber. Feed enters near the tower base and solvent near the top. Treated gas from the tower leaves the unit for further processing or use. In high operating pressure units the contact solvent may be flashed in a flash tower, where most of the absorbed hydrocarbons are separated for return to the absorber or for use as plant fuel. In other units the contacted solvent goes direct to the regenerator, where acidic gases are stripped, using a reboiler. The regenerated solvent is cooled and recirculated to the absorber. Acidic gases are cooled, condensate is separated and returned to the regenerator as reflux, and acidic gas is made available for processing.

Operating conditions: The process has been used for natural gas applications in which the H_2S content has varied from 0 to 53 mole % and the CO_2 content has varied from 1.1 to 28 mole %. Satisfactory removal of mercaptans and carbonyl sulfide is obtained for all naturally occurring mixtures of acid gases that have been found. Natural gas pipe line specifications that are readily attained are:

H_2S	below 0.25 grain/100 scf
CO_2	below 0.3 mole %
Mercaptan content	below 0.2 grain/100 scf
Total sulfur	below 1 grain/100 scf

With minor modifications to the normal plant design, the gas can be treated to LNG feedstock requirements of less than 50 ppm CO_2.

Specifications which allow 2 to 3% CO_2 can be obtained where the CO_2/H_2S ratio is high.

Absorption pressures are determined by the gas feed pressure and vary from slightly above atmospheric to 1,000 psi or more. The regenerator normally operates at near atmospheric pressure such that low-pressure steam (60 psig) is suitable for reboiler heat.

The absorber temperature varies with the operating pressure, while the solvent circulation varies with the feed gas rate and acid gas content. Circulation rates are relatively low, compared with conventional amine processes. Low corrosion rates are experienced.

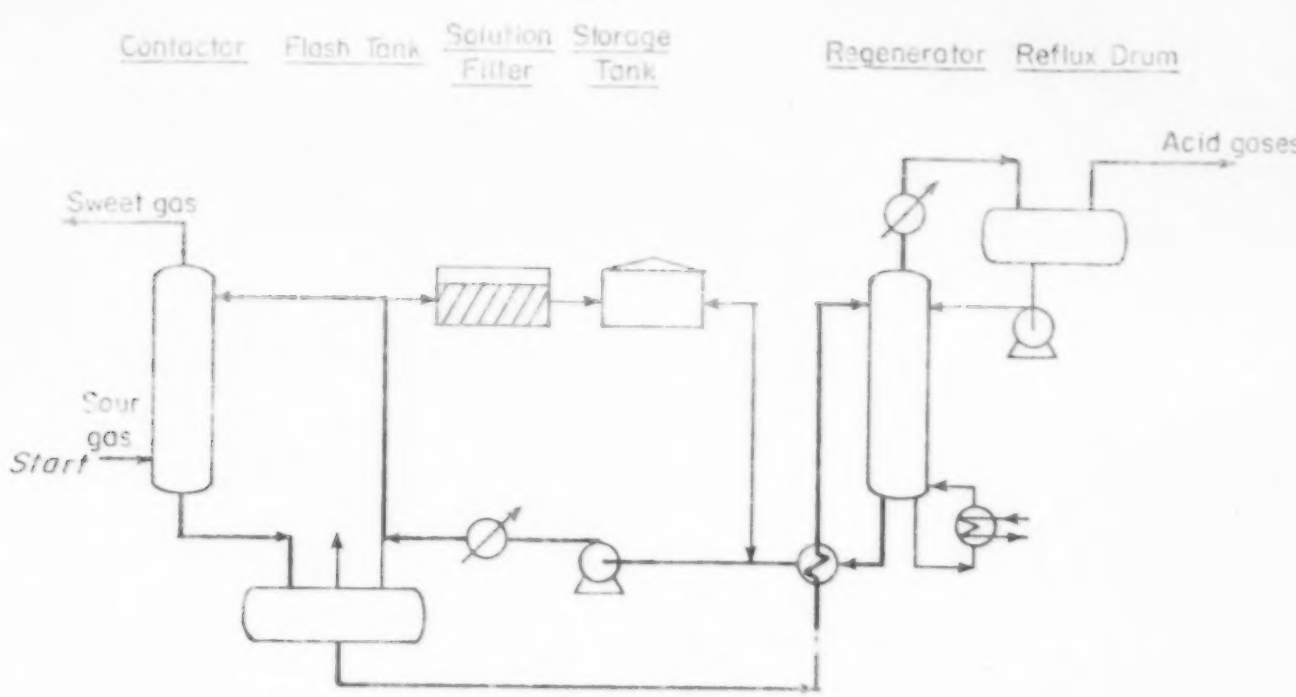
Economics: Typical requirements for utilities, per pound of acid gas removed, are:

Electricity, kWh	<0.01
LP steam (60 psig), lb.	0.8-1.6
Cooling water (or equivalent), gal.	5.4-9.8

Commercial installations: Over 100 units are in operation or under construction; about 70 percent of these are for natural gas treating.

Reference: *Hydrocarbon Processing*, Vol. 44, No. 4, pp. 137-140 (1965).

Licensing inquiries: Shell Development Co., Houston, (USA), and Shell Internationale Research Mij, B.V., The Hague (rest of world).



SNPA-DEA

Application: For sweetening raw gas streams containing a total of about 10% or more of acid gases (H_2S plus CO_2) at operating pressures of about 500 psig or higher.

Product: Natural gas streams may be treated to meet the conventional pipe line specification of ¼ grain H_2S per 100 scf maximum simultaneously with CO_2 of 2 volume % or less. The acid gases removed from the raw gas are produced at an adequate pressure and the proper temperature to serve as direct feed for a Claus-type sulfur recovery unit. No intermediate processing steps are required between the SNPA-DEA unit and the sulfur recovery unit, regardless of composition and nature of the hydrocarbons contained in the raw natural gas stream.

Description: An aqueous solution of diethanolamine (DEA) is used in concentrations determined to be economical from past commercial scale experience.

An SNPA-DEA unit is similar to a conventional DEA unit in many respects. The notable differences are: use of higher DEA concentrations, optimization of operating conditions to achieve higher than conventional loading of the rich DEA in terms of scf per gallon of solution, and specific conditioning of a slipstream of lean solution to maintain a low level of solids, corrosive products, and hydrocarbons. Incorporation of these features results in stable operation through a wide thruput range, with low foaming tendencies and, hence, high reliability and on-stream time.

Sour raw gas enters the contactor where it is scrubbed with lean DEA solution. The H_2S (and CO_2) are removed in the rich DEA leaving the contactor. Rich DEA flows to a flash tank from where dissolved gases, after being further purified, are released to fuel. From the flash tank, rich DEA is preheated and charged to the regenerator. In the regenerator the acid gases are stripped from the DEA solution, then cooled and routed to a sulfur recovery plant. Heat input to the regenerator is from low pressure steam via reboilers. Lean DEA from the regenerator is first exchanged and then cooled before returning to the contactor. Solution storage and conditioning are provided on the lean DEA stream.

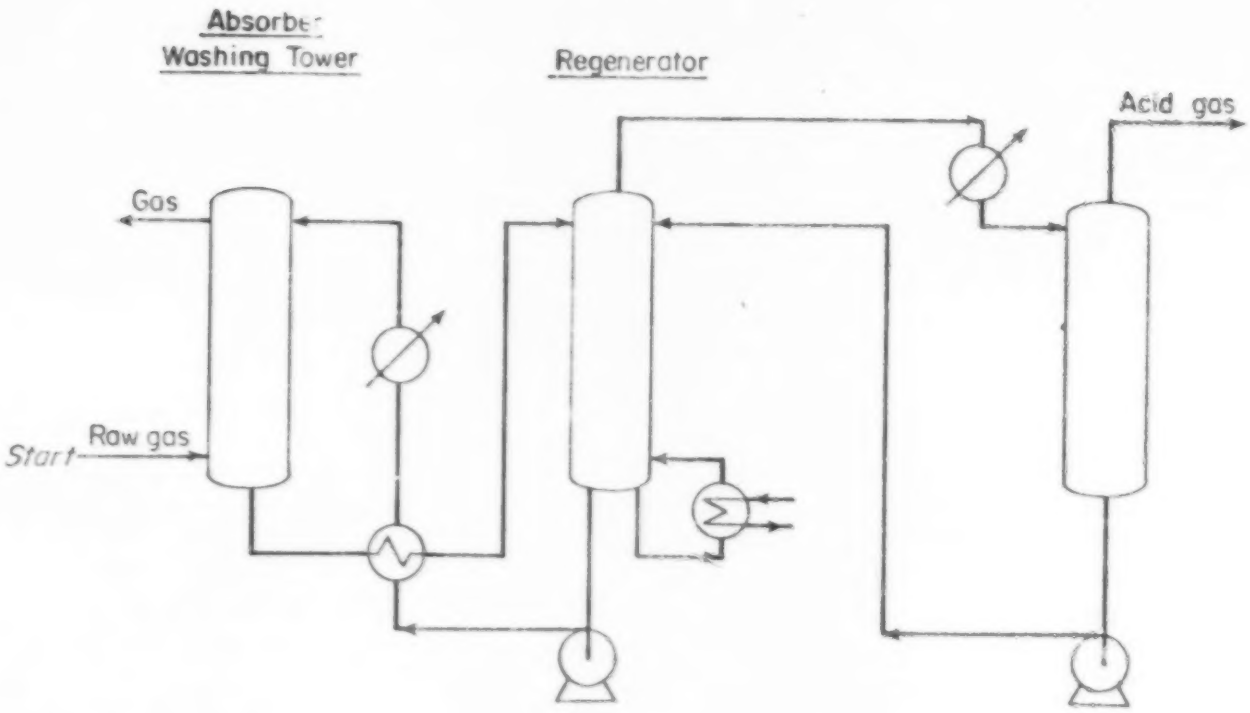
Operating conditions: Commercial units are in operation at from 600 to 1,100 psig treating raw gas streams containing from 11 to 35% acid gases. The ratio of H_2S:CO_2 ranges from 34 to 0.65 in these units.

Investment: Process factors affecting investment cost include: operating pressure, acid gas content, H_2S/CO_2 ratio and treated gas purity. The onplot investment for a battery limits units processing 220 MMscfd of natural gas at 900 psig to produce a treated gas meeting pipe line specifications will be $8-$8.5 million on a Gulf Coast basis. The total acid gas removed in this unit is 68 MMscfd with an H_2S/CO_2 ratio of 4/1.

Commercial Installations: The SNPA-DEA process is currently in use to sweeten about 3 billion scfd of raw gas, with an added 2 MMMscfd under construction.

References: Wendt, C. J., Jr., and Dailey, L. W., "Gas Treating: The SNPA Process," *Hydrocarbon Processing*, Vol. 46, No. 10, 155-157 (1967).

Licensor: The Ralph M. Parsons Co. and affiliates.



Adip

Applications: For the substantial removal (to a few ppm) of H_2S and the partial removal of incidental COS, CO_2 and mercaptans.

Charge: Natural, refinery or synthesis gas or LPG having any concentration of acid gases.

Description: The process is based on an absorption-regeneration cycle using a circulating aqueous solution of an alkanolamine which reacts with acidic gases. H_2S-containing feed is contacted countercurrently with Adip solution in an absorption or extraction column. Regenerated solution is introduced into the head of the absorption column at a normal or slightly higher temperature and leaves at the bottom of the column. Rich solution exchanges heat with regenerated solution and is fed to the regenerator. Acid gases are stripped in the regenerator, which is equipped with a steam reboiler. Cooled regenerated solution is recycled to the absorber. Acid gases removed from solution in the regenerator are cooled, thus condensing the water.

The low steam consumption normally associated with the process is further reduced when H_2S is removed from gases under pressure, because higher absorption temperatures are possible. Because of the relatively low steam consumption, savings are possible in both capital and operating costs. Initial investment is also minimized, since carbon steel is used with the non-corrosive Adip solution.

H_2S in the product can be reduced to meet stringent specifications (less than 10 ppm), thus making after-treatment unnecessary.

Operating conditions: Wide flexibility is possible in setting operating conditions. The absorber pressure is set by the pressure of the feed stream and ranges from slightly above atmospheric pressure to several hundred psi. The regenerator normally operates at slightly above atmospheric pressure, such that low-pressure (above 60 psig) steam is suitable for reboiler heat.

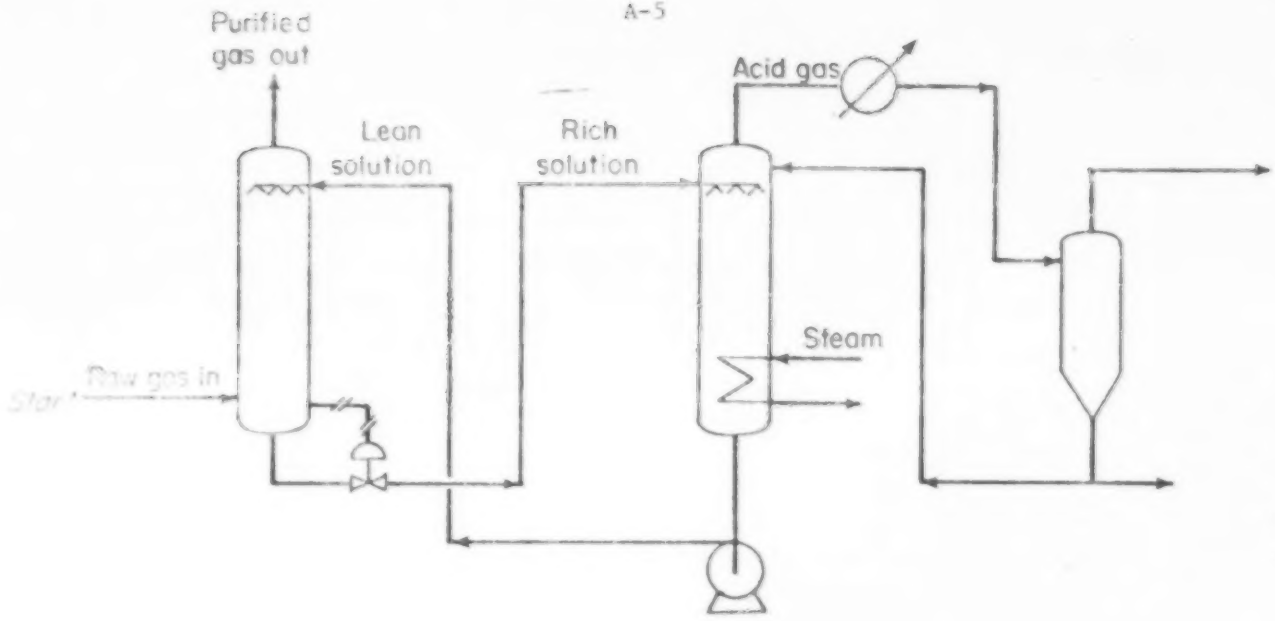
The solvent circulation rates depend on the total gas feed rate and the concentration of acidic gases in the feed.

Economics: Basis: Feed—925 metric t/d, 15.6% (vol.) H_2S and 0.3% (vol.) CO_2.
Product: 100 ppm vol. H_2S and 0.1% vol. CO_2
Plant cost: US $1 million
Solvent circulation: 200 m³/h
Utilities: L.P. steam (4.5 atm.)—450 t/sd
Electricity (incl. air cooling): 3,000 kWh/sd
Make-up water (steam condensate): 9 t/sd
Chemicals: Adip (100%, incl. mechanical losses)—70 kg/sd
Operating costs: Labor—½ operator per shift
Maintenance: 2% of capital.

Commercial installations: More than 130 units are in operation or under construction.

Reference: "Developments in Sulfinol and Adip Processes Increase Uses," *Oil and Gas International*, Vol. 10, No. 9, September 1970, pp. 109-111.

Licensing inquiries: Shell Development Co., Houston, (USA), and Shell Internationale Research Mij B.V., The Hague (rest of world).



Benfield

Applications: Removal of CO_2, H_2S and COS from sour natural gas and raw gases produced during manufacture of substitute natural gas by partial oxidation of coal or oil or by naphtha reforming. Selective removal of H_2S from CO_2 plus H_2S mixtures provides H_2S-enriched stream suitable for recovery of elemental sulfur.

Feed: Sour natural gas containing CO_2 or CO_2 and H_2S mixtures or synthetic gas containing CO_2 (and sometimes H_2S) produced by partial oxidation or reforming processes.

Product: Purified gas with H_2S reduced to pipe line purity specifications and with CO_2 removal to a few ppm.

Description: Raw gas is contacted with potassium carbonate solution containing Benfield additives at elevated pressures (100 to 2,000 psig) in an absorber column (packed or trayed) and acidic components (CO_2 and H_2S) are absorbed. The rich solution is let down to about atmospheric pressure and stripped in a regenerator tower to drive off absorbed acid gases and the regenerated lean solution then recycled to the absorber. Process conditions and flowsheet vary to meet various feed gas composition and desired product gas specifications.

Operating conditions:

Absorption Pressures—Usually 100 to 2,000 psig. No upper limit for absorber pressure.

Feed Gas Composition—Economics favored by high partial pressure of CO_2 and H_2S. In usual applications, CO_2 or CO_2 and H_2S concentrations range from 5 to 50%. Feed gas may be saturated with H_2O and may contain substantial content of higher hydrocarbons.

Feed Gas Temperatures—Not critical—usually ambient to 400°F. Heat in feed gas can be used to supply all or part of process heat requirements.

Regeneration Pressure—Atmospheric.

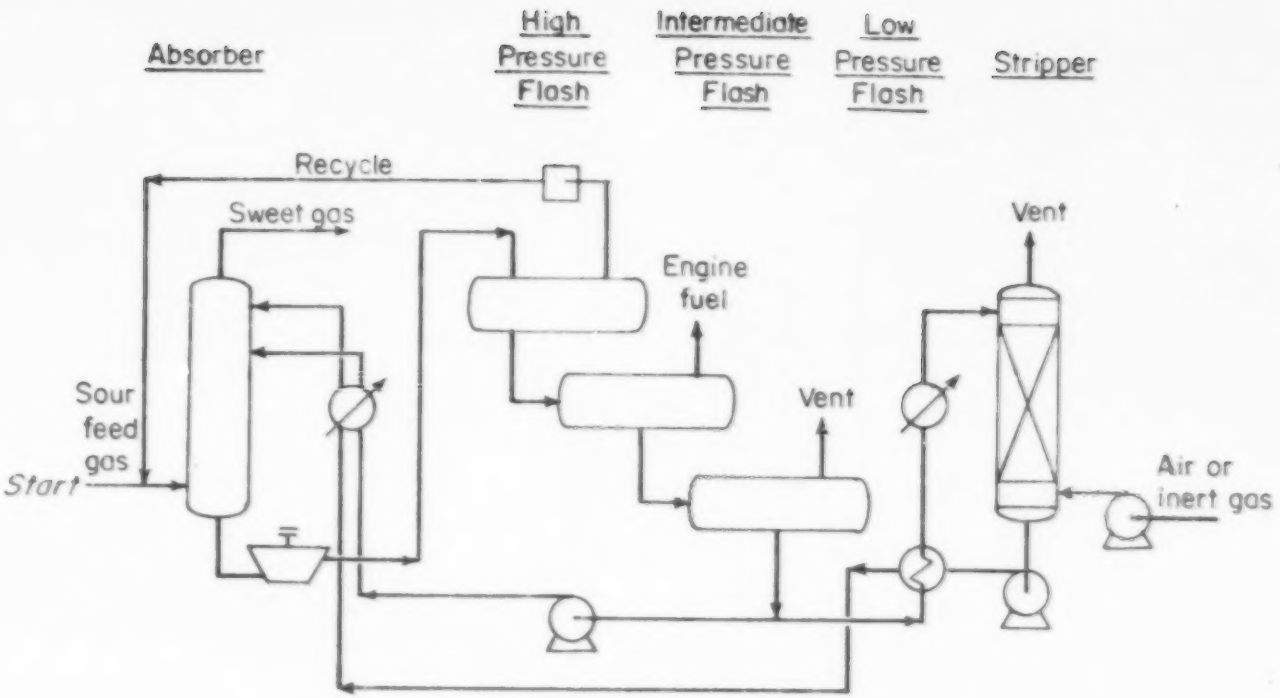
Economics: Typical capital investment (large plant) per Mscfd of CO_2 + H_2S removed: $75. Typical operating utility requirements per Mscfd of CO_2 + H_2S removed:

Regeneration Heat	70,000-130,000 Btu
Power (pumping)	1-2 kwh
Total Cooling Duty	50,000-100,000 Btu
Chemical Cost	Solution make-up for mechanical losses only—no degradation

Commercial Installations: More than 250 operating units including 18 units for natural gas sweetening and over 150 units serving substitute natural gas units (CO_2 scrubbing of reformed and partial oxidation gases).

Reference: Benson, H. E., "Hot Carbonate Plants: How Pressure Affects Costs," *Petroleum Refiner*, Vol. 40, No. 4, p. 107-108.

Licensor: The Benfield Corp., Pittsburgh, Pa.



Selexol

Application: For gas purification and removal of H_2S, CO_2, COS, mercaptans, etc., from gas streams by physical absorption. The solvent, dimethyl ether of polyethylene glycol, trade named Selexol, has strong preference for sulfur-based compounds, while retaining the capability to absorb bulk quantities of all impurities economically. It is also capable of simultaneously dehydrating to pipe line specifications.

Charge: Sour natural gas; raw product gas from the gasification of coal, oil, and light hydrocarbons; synthesis gases from steam reforming or partial oxidation; refinery gases.

Product gases: To less than 1 ppm total sulfur; CO_2 can be retained or removed as required; water to less than 7 lb./MMscf gas.

Off gases: Provide Claus plant feed stream highly enriched in sulfur compounds; pollution-free vent gases.

Description: A Selexol plant consists of an absorber together with means for desorbing by flashing and/or stripping. Recycle is sometimes included to enhance natural selectivity for sulfur compounds. Temperatures can many times be controlled without external heating or cooling, by using hydraulic turbines and heat interchange. Overall heat effects are minimized by very low heats of absorption and a specific heat of only 0.5. No solvent reclaimer is needed since there is no degradation. This, along with low vapor pressure means very low solvent losses. Solvent is non-corrosive and inherently non-foaming.

Operating conditions: Absorption of impurities is essentially proportional to their partial pressures. Feed conditions can be varied over a broad range in existing equipment. At the other end of the process, the solvent is regenerated by physical desorption, rather than chemical decomposition. Over 8 years of commercial experience shows long term maintenance-free service.

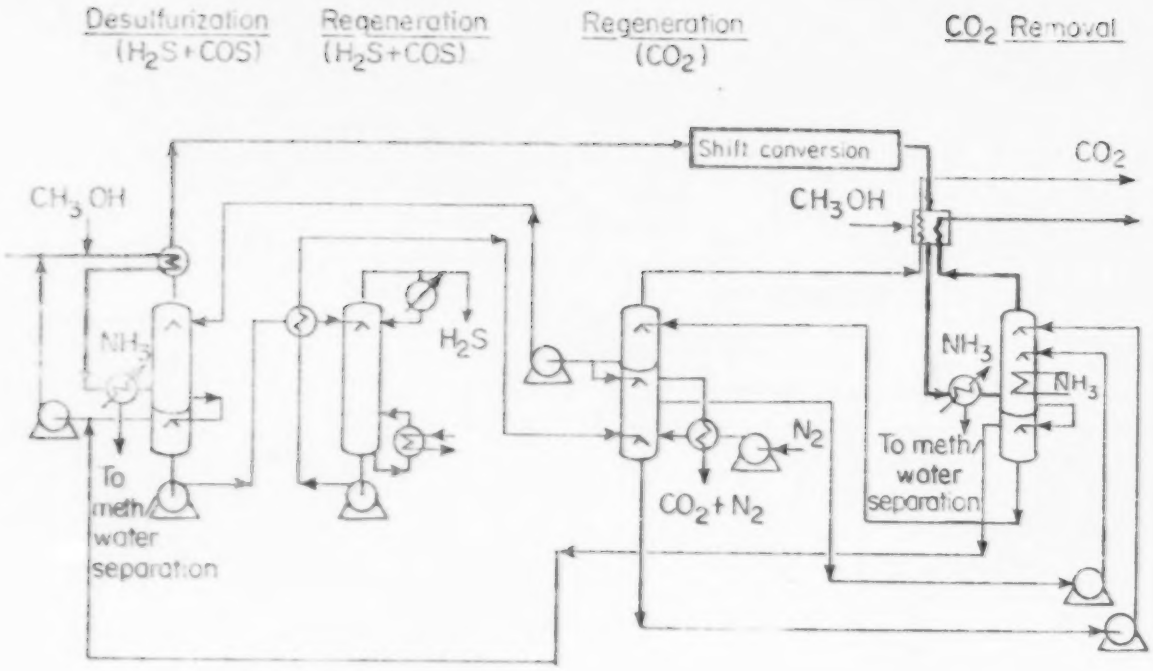
Economics (expressed as % of MEA costs): For a plant treating 100 MMscfd, operating at 1,000 psig, reducing CO_2 from 30 to 2 mole % min., and meeting H_2S spec. of 0.25 gr./100 scf.

	% of MEA
Grass roots plant	70
Direct annual operating	
Steam	10
Electricity	20
Cooling & process water	25
TOTAL	40
Indirect annual operating	75
TOTAL annual operating	50

Commercial installations: Now operating or under construction in natural gas treatment, synthesis gas purification, coal gasification purification, COS removal.

Reference: *Oil and Gas Journal*, March 20, 1967, pp. 116-118.

Licensor: Allied Chemical Corp.



Rectisol

Application: The process uses methanol as solvent in three typical applications: (1) Removal of CO_2, H_2S, NH_3, HCN, gumformers, higher hydrocarbons and other impurities from crude gas produced by coal gasification for syngas or SNG manufacture; (2) Removal of H_2S, COS and CO_2 from reformed gas, in particular from gas produced by partial oxidation of hydrocarbons, to yield synthesis gas, and (3) Integration of gas purification with low temperature plants (liquefaction and fractionation) for removal of moderate contents of acidic components.

Description (Case 2: two-stage syngas purification): Crude gas, saturated with water vapor, is indirectly cooled by cold purified gas and evaporating ammonia. Icing is prevented by the injection of methanol. The gas then enters the first absorber where sulphur compounds are removed completely by washing with methanol already charged with CO_2. After CO shift conversion and further cooling, the gas is fed into the second absorber for the removal of CO_2 down to the level required. Before leaving the plant, the purified gas is heat exchanged with the shifted gas.

Fat solvent from the first absorber, after flashing and heating, is regenerated completely in the H_2S regenerator by reboiling. After cooling, lean solvent is supplied to the second absorber top together with stripped solvent from the CO_2 regenerator. In addition, semi-stripped solvent is charged to the second absorber bottom section for bulk removal of CO_2. Fat solvent leaving the second absorber is regenerated in the CO_2 regenerator by flashing and stripping with impure nitrogen available from the oxygen unit. Solvent for desulfurization is withdrawn from the CO_2 regenerator and pumped to the first absorber top.

Co-absorbed H_2 and CO is released in the first flash stages at relatively high pressure and either returned to crude gas or used as fuel.

Refrigeration necessary for crude gas and solvent cooling can be supplied by NH_3 absorption refrigeration unit operating on waste heat.

Water introduced into solvent by crude gas is removed by treating a small bleed stream in a methanol/water distillation column.

Operating conditions: Feed: Flow—103 MMscfd (100 MMscfd H_2 and CO). Pressure—685 psig.

Desulfurization:	**Feed**	**Treated gas**	**H_2S off-gas**
CO_2, Vol. %	5.3	5.3	57.3
H_2S + COS, Vol. %	0.7	<0.1 ppm	40.1
H_2, Vol. %	44.6	45.0	—
CO, Vol. %	48.4	48.7	—
N_2+Ar, Vol. %	1.0	1.0	1.6
CO_2 removal:	**Feed**	**Treated gas**	
CO_2, Vol. %	36.1	0.1	(1 ppm possible)
H_2S + COS, Vol. %	—	—	
H_2, Vol. %	62.8	98.2	
CO, Vol. %	0.5	0.3	
N_2 + Ar, Vol. %	0.6	0.9	

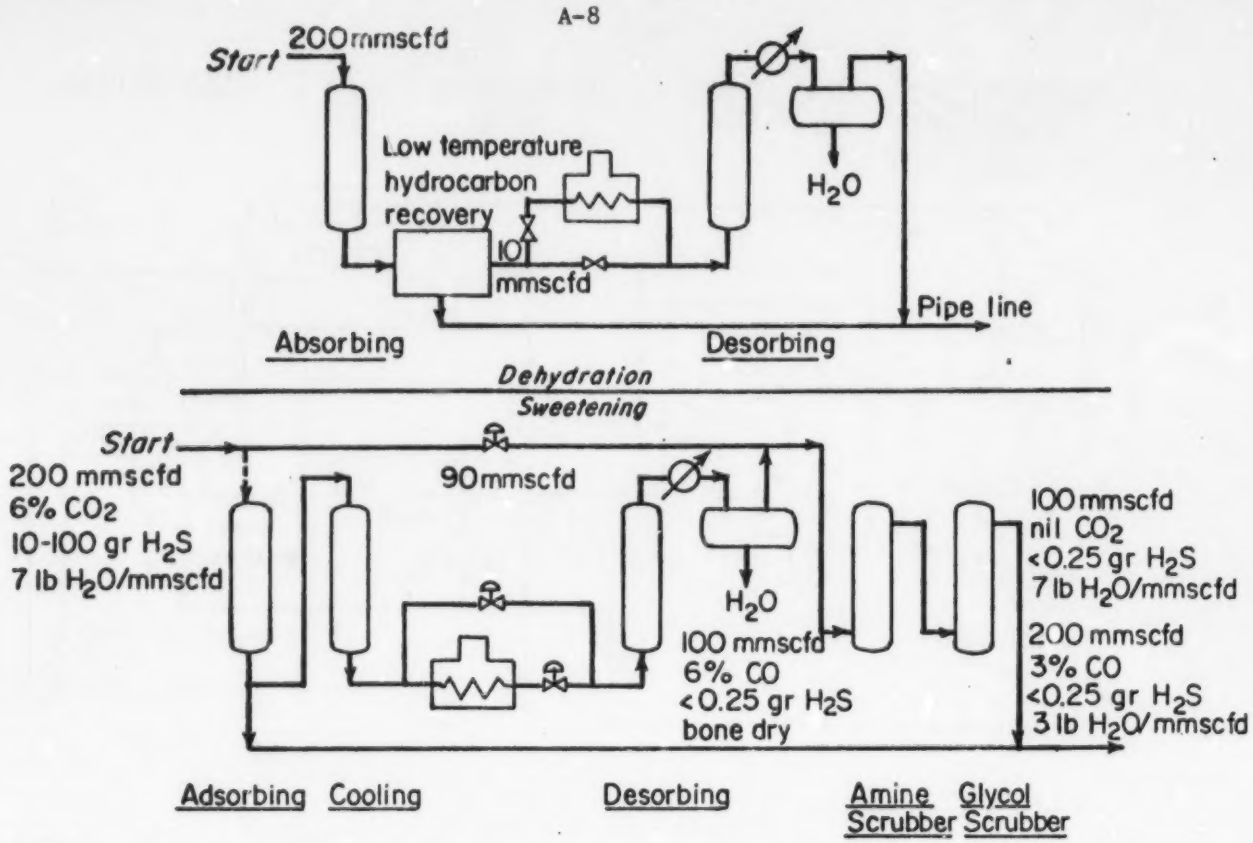
Utilities:

Power, shaft (without power recovery)	2,500 kW
Steam, 20 psig, sat'd	5.2 t/hr.
Waste heat (for refrigeration unit)	50 × 10^6 Btu/hr.
Cooling water, 75°F, 18° ΔT	2,060 m^3/hr.
Methanol	80 kg/hr.

Commercial installations: 23 operating units plus 7 in construction, total capacity more than 2 billion scfd.

References: *I. & EC*, Vol. 62 (1970), No. 7, 37/43.

Licensors: Lurgi Mineralölchnik GmbH.



Molecular sieve

Application: Processes to dehydrate and to remove carbon dioxide and sulfur compounds from natural gas.

Charge: Impure gas streams containing water, carbon dioxide and sulfur compounds.

Products: Gas meeting pipe line specifications or suitable for feeding to cryogenic processing plants and LNG plants.

Description: The processes involve two or more fixed bed adsorbers and other regeneration facilities. At least one bed is on adsorption at all times while the other bed(s) are being regenerated.

The natural gas passes through the service bed where the impure material(s) are removed to product specifications. Dry, treated regeneration gas is heated to 400-600° F in a cooling adsorber and/or a heater, then fed counter current to normal flow through the adsorber bed being regenerated. Impure gas from the bed being desorbed is cooled, liquid water is separated, and the stream fed to the product line, used for fuel, or goes on for further treating.

A typical flow arrangement for carbon dioxide removal is similar to that shown for sweetening except that no further treating and drying is usually needed.

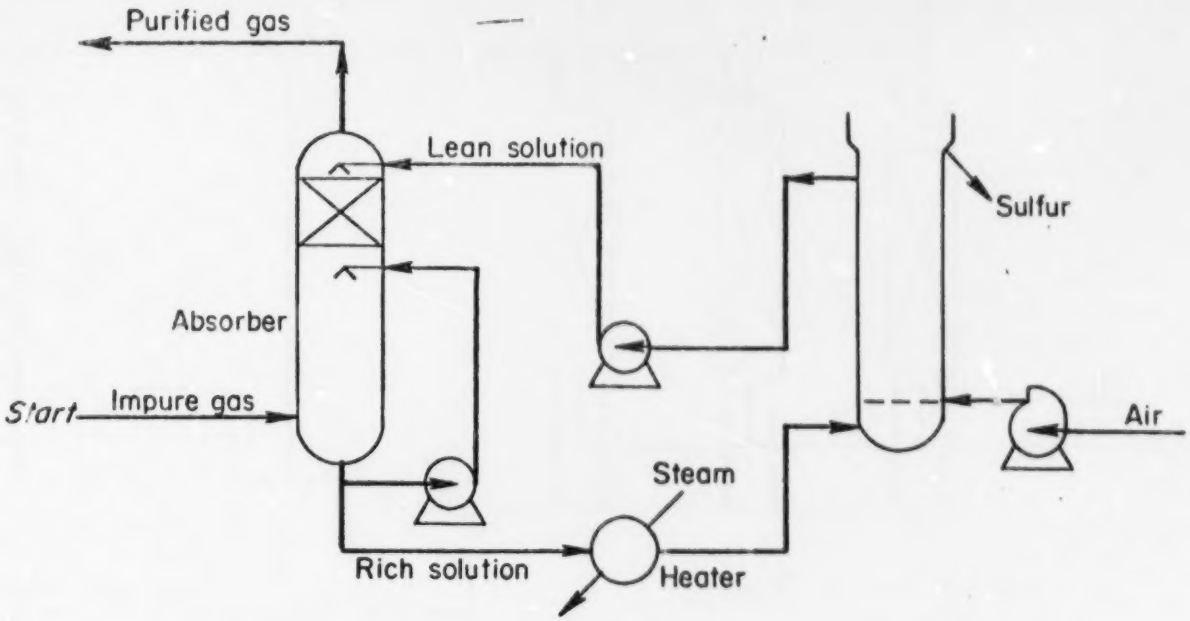
Selection of the appropriate type molecular sieve depends on impurities to be removed. Type 4A is most commonly used for dehydration and Type 4A-LNG for carbon dioxide. Several types are used for desulfurization depending on the kinds of sulfur compounds and their concentrations to be removed. Sieve life ranges from two to five years for desulfurization and carbon dioxide removal, and from three to seven years for dehydration.

Molecular sieves used for drying cryogenic plant feed can be used also for drying out the plant during shutdown and before startups.

Economics: Unit size is dependent on the concentration of impurities in the feed and other factors. Generally, molecular sieves are used for sweetening when carbon dioxide can be left in the product. Their use for dehydration depends on the required dew point and normally occurs when the dew point must be −40° F or below. Carbon dioxide removal with molecular sieves is most attractive when the product must have a very low CO_2 content and the feed has 1.5% (mol) CO_2 or less.

Commercial applications: More than 12 units are used for sweetening over two billion scfd natural gas. All cryogenic gas processing plants in the USA except two use molecular sieve dehydration. Twenty-nine LNG prepurifiers are in operation and others are in the design or construction stage.

Contributor: Union Carbide Corp., Linde Div.



Giammarco Vetrocoke—sulfur

Application: For the continuous removal of hydrogen sulfide from natural gas or synthesis gases.

Description: The Giammarco Vetrocoke (H_2S) process for the removal of H_2S continuously scrubs sour gas with an alkali arsenates and arsenites solution. Sodium carbonate, being relatively inexpensive, is the alkali usually applied for the removal of large quantities of sulfur. The successive reactions occurring are:

$$Na_3AsO_3 + 3\,H_2S = Na_3AsS_3 + 3\,H_2O \quad (1)$$

$$Na_3AsS_3 + 3\,Na_3AsO_4 = 3\,Na_3AsO_3S + Na_3AsO_3 \quad (2)$$

$$Na_3AsO_3S = Na_3AsO_4 + S \quad (3)$$

$$Na_3AsO_3 + \tfrac{1}{2}\,O_2 = Na_3AsO_4 \quad (4)$$

Sour gas enters the base of the absorber column at pressures up to and above 75 ats. g., depending on wellhead gas conditions. A counterflow stream of Vetrocoke solution scrubs the H_2S to a level of 0.5 ppm or less. The sweetened gas leaving the absorber is cooled to reduce the load on the downstream dehydration plant. The condensate removed takes with it most of the carryover. The absorption reaction, Equation 1, gives rise to sodium thioarsenite which has a low vapor pressure of H_2S and allows a high purity gas to be obtained by straight countercurrent absorption.

The thioarsenite formed is slowly converted to monothioarsenate and arsenite by a "digestion reaction," Equation 2, which occurs in absorber and in the subsequent oxidizing column. The monothioarsenite formed has an even lower vapor pressure of H_2S.

Mono-thioarsenate, being more soluble, helps keep the sulfur in solution.

The solution leaving the base of the absorber passes to an air-blown oxidizing column working at atmospheric pressure and around 40°C. This vessel is open to atmosphere at the top. Under the oxidizing conditions, the mono-thioarsenate decomposes to arsenite and elemental sulfur. Elemental sulfur is removed overhead by froth flotation, vacuum filtered and washed. The oxidizing reaction also re-establishes the original Vetrocoke solution balance by oxidizing some arsenite to arsenate.

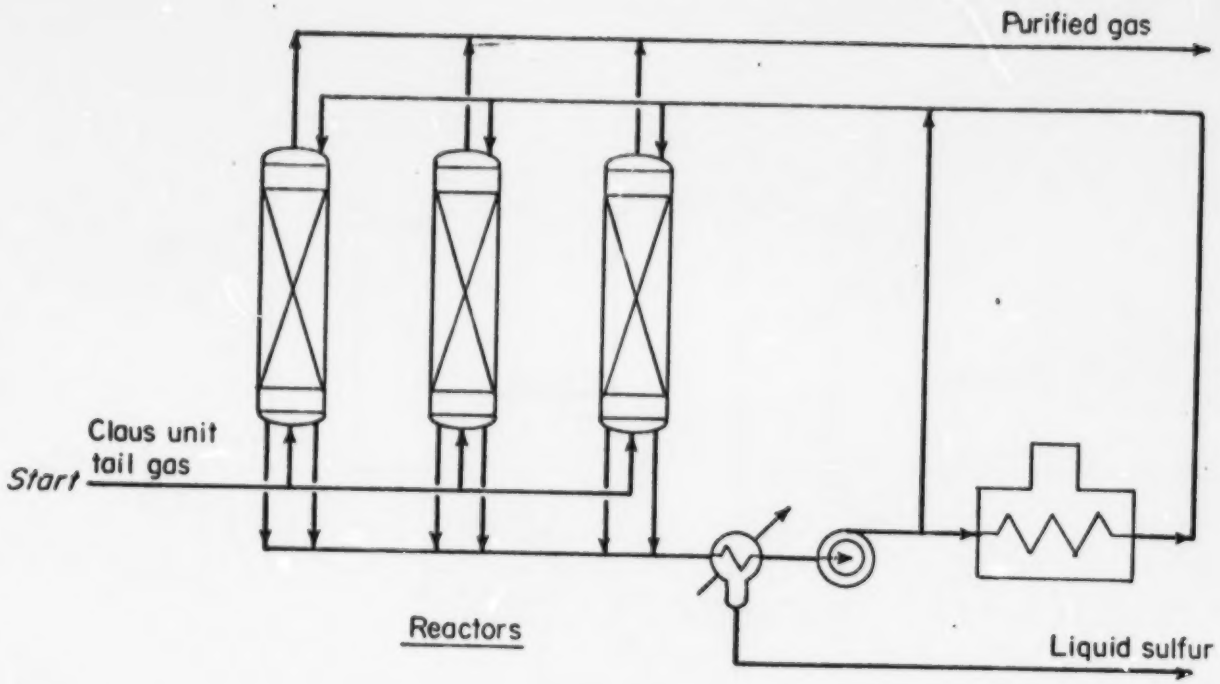
Operating conditions: The dual function of the oxidizing tower limits the variation possible in the air flow to the oxidizer because flotation process would be impaired and a constant flow of solution to the absorber is possible only at constant air rates. It is not practical to control arsenate formation solely by the depth of solution aeration. A small amount of catalyst is added to promote and control arsenate formation. This also reduces oxidizer size.

Commercial installations: Approximately 30.

Economics: Battery limits capital cost of a 100 MMscfd plant (in the United Kingdom) is approximately $600,000. This plant removes H_2S from inlet concentration of 600 ppm to outlet of ½ ppm. Utility costs are approximately 0.193 cents/MM Btu of treated gas.

Reference: Maddox, R. N. and Burns, M. D., "Liquid Absorption-Oxidation Processes," *Oil and Gas Journal*, Vol. 66, No. 23, p. 90-91, (1968).

Contributor: Power-Gas Ltd.



Sulfreen

Application: Desulfurization of residue gas.

Charge: Claus unit tail gas.

Products: Liquid sulfur.

Description: The process is essentially an extension of the Claus process, except that H_2S and SO_2 are made to react at temperatures below the sulfur dew point of the reaction gas mixture:

$$2\,H_2S + SO_2 \longrightarrow 3\,S + 2\,H_2O + 35\,Kcal$$

Since equilibrium conversion becomes more complete as temperature is lowered, substantially higher sulfur recovery is possible than in a normal Claus plant. The reaction takes place in the presence of a catalyst, either alumina or special activated carbon.

Sulfur formed is adsorbed on the catalyst which eventually becomes saturated, requiring periodic regeneration by desorption of sulfur with hot gas.

The process reduces entrained sulfur to a minimum, as the catalyst acts as a very effective adsorbent for liquid sulfur. COS and CS_2 are not affected.

Unit operation is exceedingly simple and differs only slightly from that of a Claus unit. Since only solid adsorbents are used and no liquids except sulfur condense, the process is free of liquid waste disposal problems. Sulfur produced is bright yellow and of 99.9% purity.

A unit may consist of three reactors, two in adsorption and one in desorption service. The number of reactors is determined strictly by economic considerations. Desorption of sulfur is effected by means of hot gas in a closed cycle. Desorption gas, containing liquid sulfur is combined with Claus produced sulfur. Since produced sulfur is of the same quality no product contamination exists.

An alternate of the Sulfreen process involving two-stage treatment can provide over-all recoveries exceeding 99%. A two-stage Sulfreen unit consists of two catalytic beds in series. In the first bed H_2S and SO_2 form sulfur according to the Claus reaction; however, the ratio of H_2S/SO_2 is adjusted in such a manner that essentially all of the SO_2 is consumed and the effluent gas contains only H_2S. After addition of air to the first stage effluent, H_2S is oxidized directly to sulfur in the second stage.

With a 95% conversion in the Claus plant and COS and CS_2 content reducing the yield by 0.5%, an over-all yield around 99% (or higher with the alternate) can be obtained, with either catalyst.

Operating conditions: As all processes based on the Claus reaction, a control with an optimizer of the H_2S/SO_2 ratio is required in the reaction gas mixture at or near the stoichiometric proportion of 2:1 for optimum results. Pressure drop through the unit is in the order of 1.4-2 psi. Catalyst life expected: at least 4 years.

Investment/operating costs: Use of alumina catalyst permits carbon steel construction and gives a lower cost for the unit. Battery limits capital cost of a unit for a 1,000 ltpd sulfur plant will be around $2 million.

Utilities consumption will be as follows:

Electricity—650 Kwh
Boiler feed water—10 U.S. gpm
Fuel gas—0.55 MMscfd

Commercial installations: 2 onstream: One in France (1,000-t/d sulfur plant) and one in Canada (4,000-t/d sulfur plant). 3 in construction.

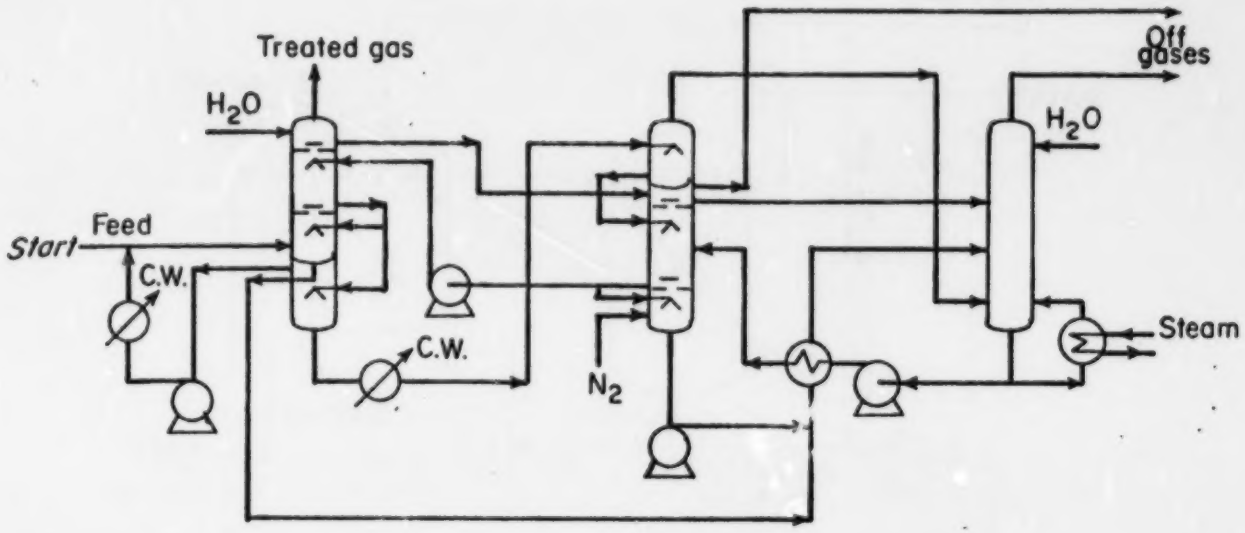
Reference: Guyot, G. and Martin, J. F., "The Sulfreen Process," Canadian NGPA, June 11, 1971.

Licensor: SNPA/Lurgi; The R. M. Parsons Co., engineering.

APPENDIX B

DETAILED DESCRIPTION OF MINOR (LESSER KNOWN) H_2S REMOVAL PROCESSES

Absorber — Stripper — Solvent Dryer



Purisol

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Application: Removal of acid gases from syngas and natural gas streams using physical absorption in N-Methyl-Pyrrolidone (NMP). Three typical applications for high pressure gases:

(1) Removal of high contents to low residual level,

(2) Bulk removal of acedic components down to moderate product purity using a simplified flash regenerator system,

(3) Selective removal of H_2S.

Process description: (Case 1, above) cooled raw gas saturated with water vapor enters the CO_2 absorber where it is dehydrated with rich NMP and then washed with regenerated NMP. Entrained NMP is removed from treated gas by water wash.

Rich solvent is first regenerated by two-stage flashing to atmospheric pressure. Co-absorbed H_2 and CO are degassed at relatively high pressure and recompressed into raw gas. Residual CO_2 is removed from NMP by air or waste nitrogen stripping. CO_2 and stripped gas are discharged via water wash.

The solvent drier is fed with NMP/water mixtures from dehydration and water wash sections and separates water and NMP by distillation with surplus water discharged from the top with the off-gas and dried NMP from the bottom. This column also removes NMP from off-gas from the second flash stage.

Operating conditions:

Feed conditions:

Flow	100 MMscfd
Pressure	1,070 psig
Temperature	110° F

Analyses:

	Feed	Treated gas
H_2, % vol.	64.53	96.44
CO_2, % vol.	33.15	0.10
CO, % vol.	1.50	2.24
C_1, % vol.	0.44	0.59
N_2 + Ar, % Vol.	0.38	0.63

Utilities:

El. power, at the shaft (without power recovery)	2,100 kW
Steam, 45 psig, sat'd	1.7 t/hr.
Cooling water, 75° F	300 m³/hr.
Condensate	1.3 t/hr.
NMP excl. leakage	3 kg/hr.

Commercial installations: 4 plants with a total thruput of 420 MMscfd are in operation; 2 for high pressure hydrogen manufacture, 2 for natural gas treating.

Reference: Hochgesand, G., "Rectisol and Purisol," *Industrial and Engineering Chemistry*, Vol. 62 (1970), No. 7, p. 37/43.

Licensor: Lurgi Mineralöltechnik GmbH.

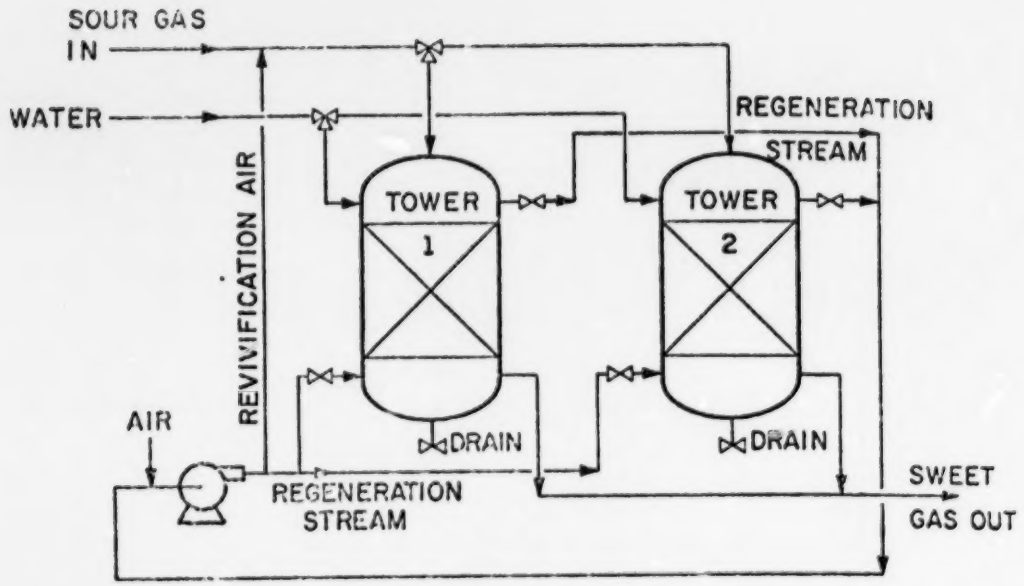


FIGURE B-2. TYPICAL IRON OXIDE PROCESS FLOW SHEET
(Courtesy: Campbell Petroleum Series and Dr. R. N. Maddox)

IRON OXIDE (SPONGE) PROCESS

Application:

Removal of H_2S from gases using the solid bed reaction of H_2S with iron oxide (Fe_2O_3). The reaction is regenerative.

$$2Fe_2O_3 + 6H_2S \quad 2Fe_2S_3 + gH_2O$$

$$2Fe_2S_3 + 3O_2 \quad 2Fe_2O_3 + 6S$$

Process Description:

A typical flow scheme using two towers is shown above. The use of more than two towers is possible. In a 2-tower process, one of the towers would be on stream removing H_2S from the sour gas while the second tower would either be in a regenerative cycle or having the iron sponge bed replaced. Both continuous and periodic regeneration are used. A bed is discarded when the H_2S content of sweet gas is unacceptable. The system is most suitable for low H_2S concentrations and/or low gas rates and will operate satisfactorily at low pressures. For certain applications, capital costs about 1/4 of MES system costs.

Operating Conditions:

Feed Conditions:

Flow. No minimum flow

Pressure. Any pressure

Temperature. About 80° F

Commercial Installations:

More than 200 units are in use in the U.S.

Reference:

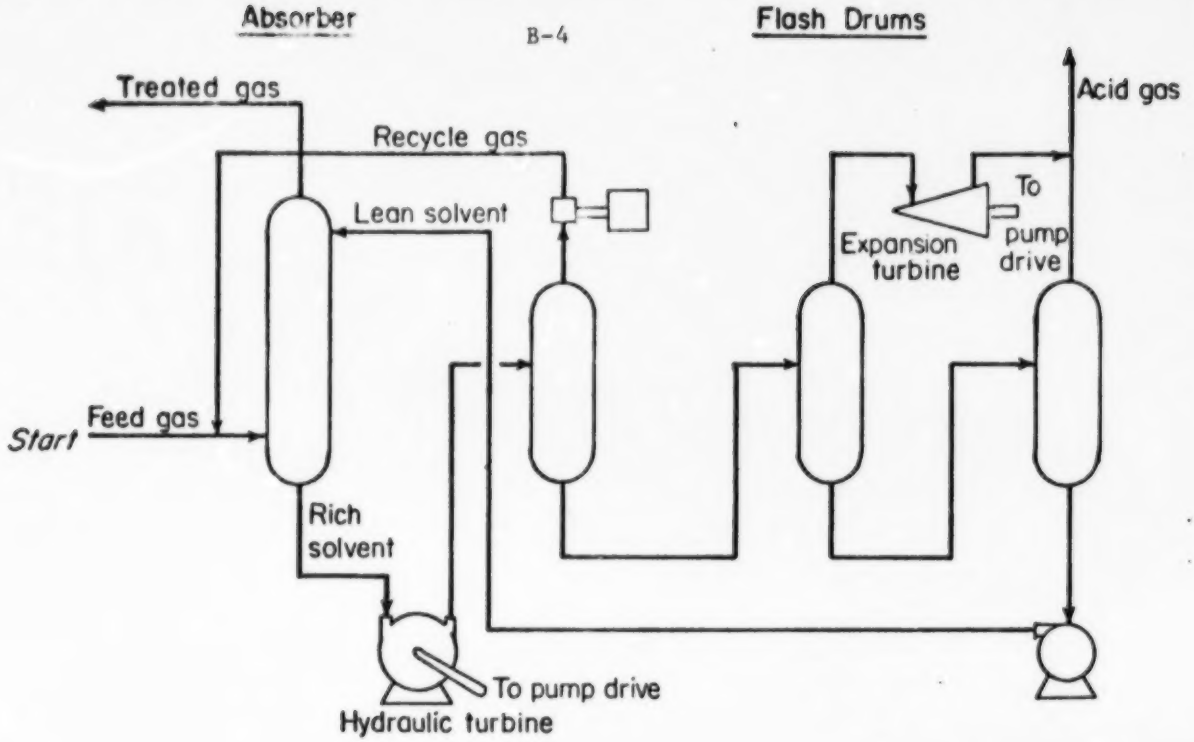
Maddox, R. N., Gas and Liquid Sweetening, John M. Campbell Co., Norman, Oklahoma 73069 (1974).

Manufacturers:

(1) National Tank Company, Tulsa, Oklahoma

(2) Fish Engineering and Construction, Inc.

The process is nonproprietory.



Fluor Solvent

Application: For the removal of high concentrations of acidic impurities, CO_2, and H_2S, from natural or synthetic gas streams.

Product: Plant designs are tailored to meet the purity levels of CO_2 and H_2S needed in each specific situation.

Description: The Fluor Solvent Process employs an anhydrous organic compound, propylene carbonate, to remove CO_2 and H_2S from natural gas streams. The use of this high capacity solvent, which absorbs acid gas by physical solution, permits solvent regeneration simply by pressure letdown of the rich solvent, usually without the application of heat.

In general, this process is best suited for cases where the combined CO_2 plus H_2S partial pressure in the feed gas is high, about 75 psi or higher. In addition, the use of this process is favored by low heavy hydrocarbon content.

The processing arrangement selected for any particular installation will depend upon a number of factors. These include the degree of purification required for both CO_2 and H_2S, concentration of both CO_2 and H_2S in the feed gas, operating pressure, etc. Since solvent carrying capacity is increased at reduced temperatures, solvent temperatures below ambient are usually used to cut circulation rate to a minimum. Often, the expansion of the acidic constituents through the plant furnishes sufficient free refrigeration to make this possible. At other times it has been found advantageous to install auxiliary refrigeration facilities to permit lower circulation rates with attendant reduction in equipment sizes. Split-stream schemes can be applied to certain situations and other techniques may be applied to assure the production of sales gas containing 0.25 grain H_2S/100 scf. At other times simple atmospheric flashing or vacuum flashing will be the preferred method of solvent regeneration. Hydraulic turbines in the rich solvent, and gas expansion turbines on flash gas streams separated at intermediate pressures, are common items in Fluor Solvent plants. Both these devices conserve energy and reduce requirements for outside refrigeration.

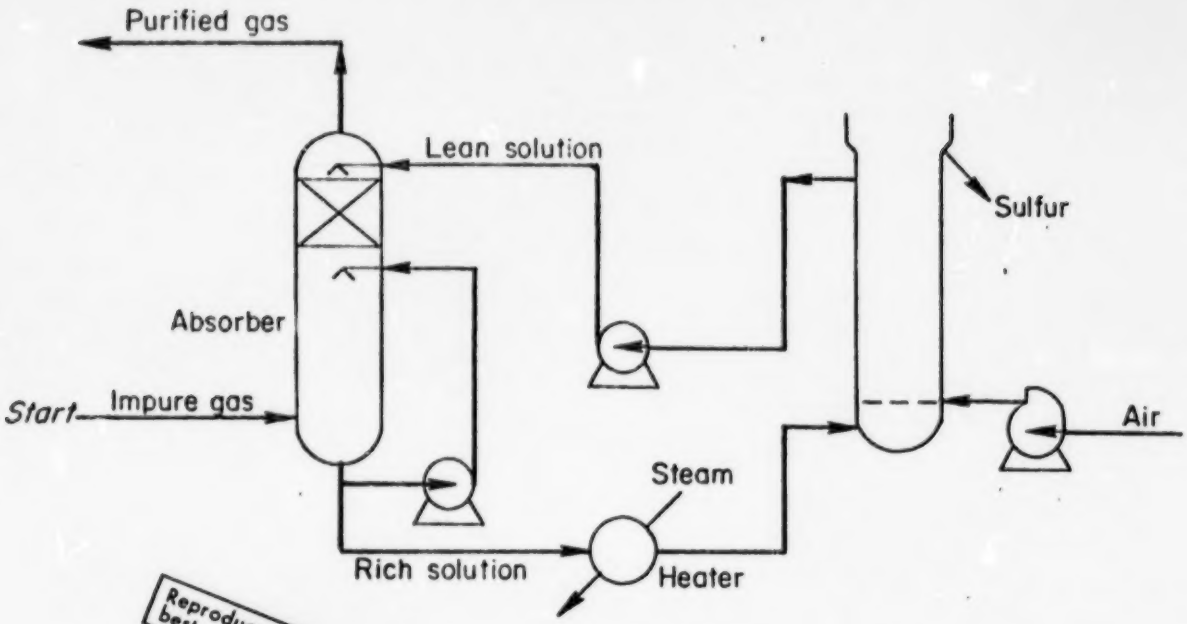
Extended operation of this process over a 12-year period has demonstrated conclusively that solvent reclaimers are unnecessary. The solvent breakdown rate is virtually nil. Several plants have demonstrated total solvent losses of 1 pound per million standard cubic feet of feed gas, other plants have demonstrated even lower losses.

Sidestream distillation or other special equipment for water elimination is not required. By proper process design, water content of the solvent is kept at 1 percent or below. Carbon steel is a suitable material of construction for all equipment and piping in this process.

Commercial Installations: The process is now in use in a total of 10 plants, 7 on natural gas, 1 in ammonia production and 2 in hydrogen production.

Reference: Buckingham, P. A. "Fluor Solvent Process Plants: How They Are Working," *Hydrocarbon Processing*, Vol. 43, No. 4, 113-116, (1964).

Licensor: Fluor Engineers and Constructors, Inc.



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Giammarco Vetrocoke—sulfur

Application: For the continuous removal of hydrogen sulfide from natural gas or synthesis gases.

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Sour gas enters the base of the absorber column at pressures up to and above 75 ats. g., depending on wellhead gas conditions. A counterflow stream of Vetrocoke solution scrubs the H_2S to a level of 0.5 ppm or less. The sweetened gas leaving the absorber is cooled to reduce the load on the downstream dehydration plant. The condensate removed takes with it most of the carryover. The absorption reaction, Equation 1, gives rise to sodium thioarsenite which has a low vapor pressure of H_2S and allows a high purity gas to be obtained by straight countercurrent absorption.

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Operating conditions: The dual function of the oxidizing tower limits the variation possible in the air flow to the oxidizer because flotation process would be impaired and a constant flow of solution to the absorber is possible only at constant air rates. It is not practical to control arsenate formation solely by the depth of solution aeration. A small amount of catalyst is added to promote and control arsenate formation. This also reduces oxidizer size.

Commercial installations: Approximately 30.

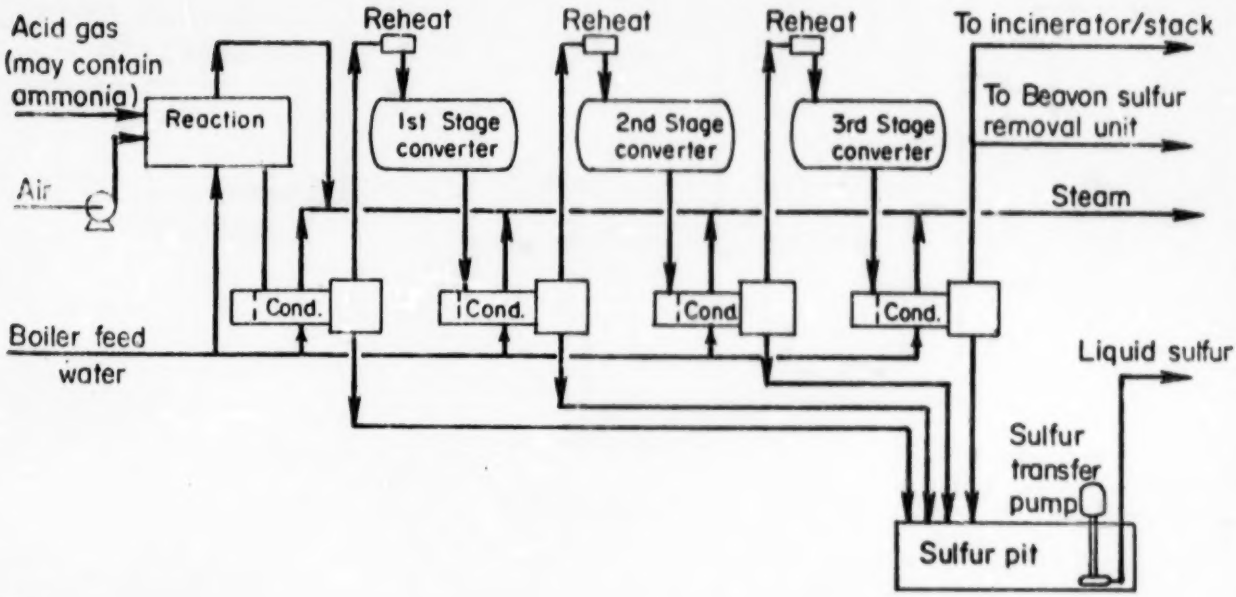
Economics: Battery limits capital cost of a 100 MMscfd plant (in the United Kingdom) is approximately $600,000. This plant removes H_2S from inlet concentration of 600 ppm to outlet of ½ ppm. Utility costs are approximately 0.193 cents/MM Btu of treated gas.

Reference: Maddox, R. N. and Burns, M. D., "Liquid Absorption-Oxidation Processes," *Oil and Gas Journal*, Vol. 66, No. 23, p. 90-91, (1968).

Contributor: Power-Gas Ltd.

APPENDIX C

DESCRIPTION OF SULFUR PRODUCTION PROCESSES



Claus

Application: Conversion of hydrogen sulfide to high purity sulfur.

Feedstock: Hydrogen sulfide gas streams from gas processing and refinery operations.

Product: High purity elemental sulfur.

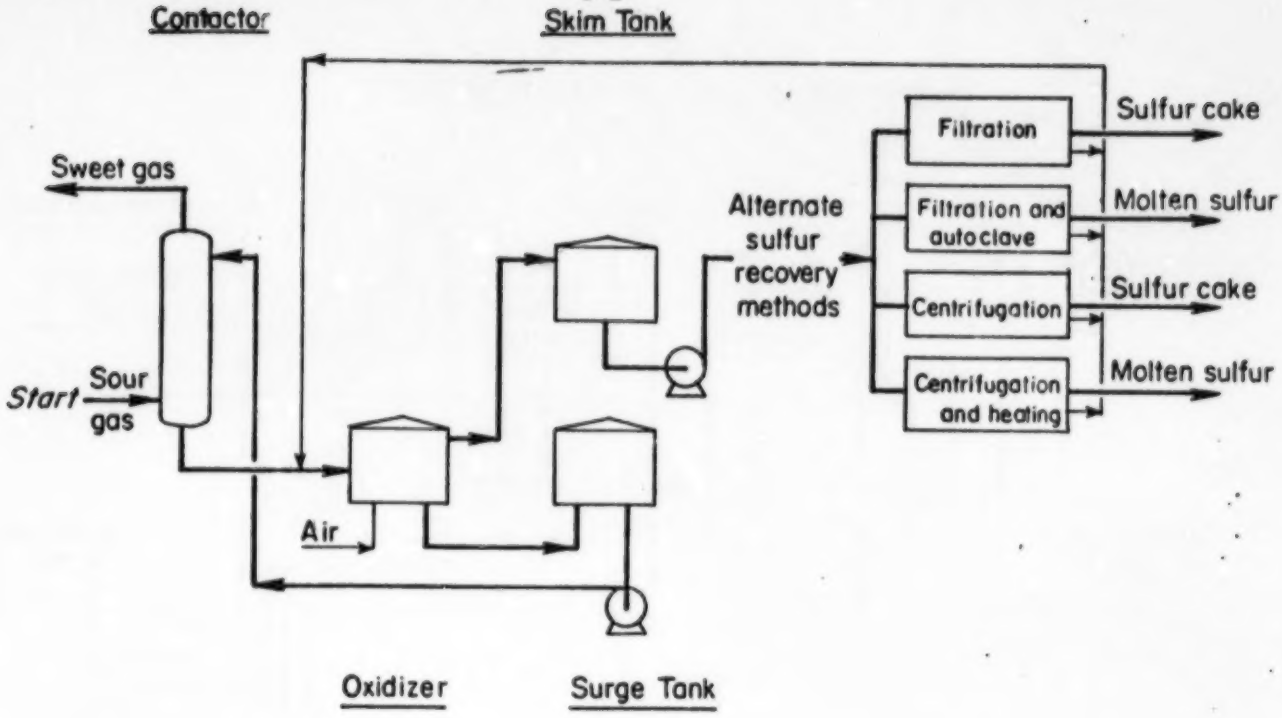
Description: The hydrogen sulfide containing acid gas stream, which may originate in a conventional amine unit or similar process, is fed to a reaction furnace where it is burned with sufficient air to satisfy the stoichiometry of the Claus reaction. The hot reaction gases are cooled in the steam generating section of the reaction furnace and then further cooled in the first condenser where sulfur produced in the reaction furnace is removed. After reheating, the gases enter the first catalytic converter where additional sulfur is formed, which is condensed in the second condenser. In the process shown three catalytic conversion stages are used. However, in some cases it may be economical to add a fourth stage. Depending on the hydrogen sulfide concentration in the acid gas fed to the unit, the number of catalytic stages and the quality of the catalyst used, conversion efficiencies of up to 98 percent can be attained.

With proper modifications the process is suitable for the treatment of acid gases containing hydrogen sulfide over a wide range of concentrations. In addition, the process can be designed so that the presence of impurities, such as hydrocarbons and ammonia, in the acid gas stream has no harmful effect on plant performance and sulfur product quality. There are many units in operation which process refinery gas streams containing appreciable amounts of ammonia. This feature is of particular importance in view of pollution control requirements which necessitate essentially complete removal of hydrogen sulfide from all gaseous and liquid refinery streams and conversion to elemental sulfur before disposal as waste.

Under the conditions prevailing in the reaction furnace, formation of some carbonyl sulfide (COS) and carbon disulfide (CS_2) is inevitable if the acid gas contains CO_2 and hydrocarbons. Although the amounts of COS and CS_2 formed are relatively small, especially if the hydrocarbon content of the acid gas is low, they are significant as potential air pollutants. A special catalyst may be placed in one or several of the catalytic converters to largely hydrolyze COS and CS_2 to H_2S and CO_2, and thus to prevent these compounds from escaping to the atmosphere. The modified process emphasizes maximum conversion efficiency and the highest degree of reliability at low capital investment and operating costs. The high conversion efficiency minimizes expenditures for tail gas desulfurization.

Operating conditions: The process has been applied to acid gas streams containing from 15 to 100 percent H_2S in capacities from 5 to 1,500 long tons per day. The smallest units are skidmounted.

Contributor: Ralph M. Parsons Co.



Stretford

Application: For the sweetening of natural and industrial gases by the complete removal of hydrogen sulfide and the partial removal of organic sulfur compounds.

Product: An H_2S content of 1 ppmv can be attained in the treated gas at operating pressures through the range of atmospheric to pipe line pressure. Sulfur of 99% purity can be produced molten or as a cake. Particle sizes range from 0.5 to 25 microns. It has found use in agricultural insecticides, plus all normal commercial outlets for elemental sulfur.

Description: The gas is washed with an aqueous solution containing sodium carbonate, sodium vanadate, anthraquinone disulfonic acid. The solution reaches an equilibrium with respect to the CO_2 in the gas and only relatively small amounts of CO_2 are removed by the process. Thus, the process represents an economic route for sweetening a sour CO_2 containing gas with much less shinkage than that associated with amine based processes.

The sour gas is countercurrently washed with regenerated liquor. The hydrogen sulfide dissolves in the alkaline solution and is removed to any desired level. The hydrosulfide formed reacts with the 5-valent state vanadium and is oxidized to elemental sulfur. The liquor is regenerated by air blowing, and the reduced vanadium is restored to the 5-valent state through a mechanism involving oxygen transfer via the ADA. The sulfur is removed by froth flotation and the scum produced can be processed several ways depending on the desired end product, total sulfur production, and utilities cost. For large sulfur production rates, one or more stages of centrifuging followed by heating are often economic. For lower sulfur capacities, simple filtration of the sulfur scum may be used.

Operating conditions: The reactions upon which this process is based are essentially insensitive to pressure. Thus, complete removal of H_2S is attained equally at a few inches of pressure as well as at the 1,000-psig level. Operating temperatures throughout the unit are in the range of ambient to 120° F and result in an operating environment remarkably free of corrosion tendencies.

Investment: Process factors affecting investment cost include: operating pressure, H_2S content of feed gas, and disposition of sulfur product. The onplot investment for a battery limits unit processing 15 MMscfd of natural gas at 30 psig, and reducing its H_2S content from 200 grains per 100 scf to ¼ grain per 100 scf will be $600,000-$700,000 on a West Coast basis. CO_2 content of this raw natural gas is 6 vol. % and remains in treated gas product. Produced sulfur is discharged as a damp cake for disposal at no value.

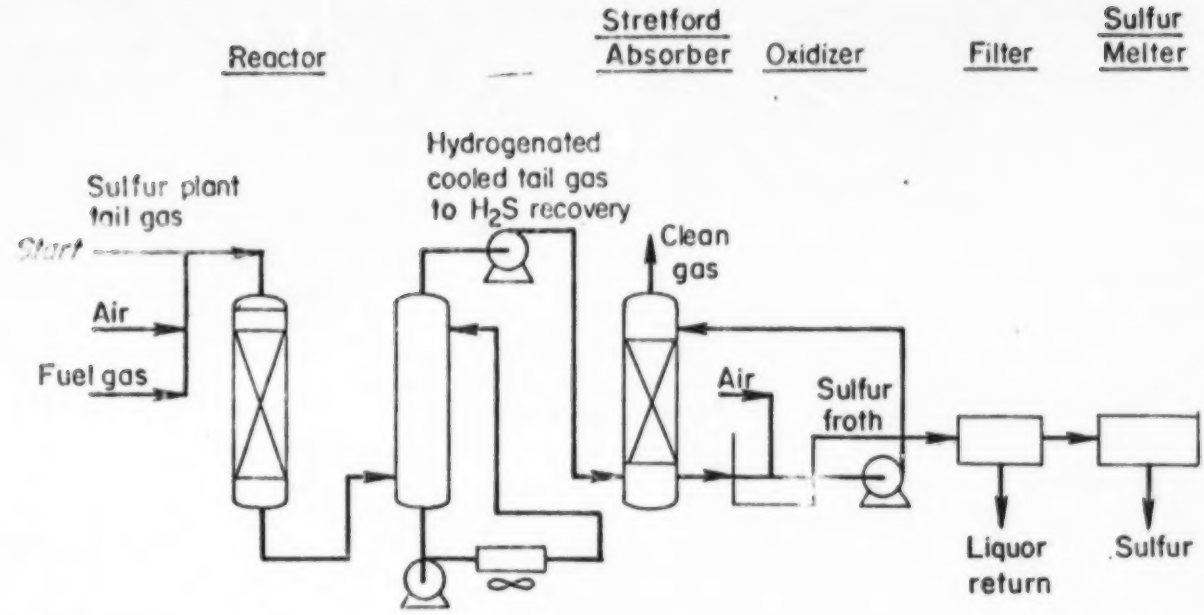
Commercial installations: 55 Stretford units are currently in operation, with capacities ranging from 100 Mscfd to 90 MMscfd.

Reference: Ellwood, P., "Meta-Vanadates Scrub Manufactured Gas," *Chemical Engineering*, Vol. 71, No. 15, July 20, p. 128-130, (1964).

Licensor. International Consultancy Services, British Gas Corp.

APPENDIX D

DESCRIPTION OF TAIL GAS CLEANUP PROCESSES



Beavon

Application: Purification of sulfur plant tail gas to meet air pollution standards.

Feed: Tail gas from Claus sulfur recovery unit.

Description: In the first portion of the process, all sulfur compounds in the Claus tail gas (SO_2, S_x, COS, CS_2) are converted to H_2S. The tail gas is heated to reaction temperature by mixing with the hot combustion products of fuel gas and air. This combustion may be carried out with a deficiency of air if the tail gas does not contain sufficient H_2 and CO to reduce all of the SO_2 and S_x to H_2S. The heated gas mixture is then passed through a catalyst bed in which all sulfur compounds are converted to H_2S by hydrogenation and hydrolysis. The hydrogenated gas stream is cooled by direct contact with a slightly alkaline buffer solution before entering the H_2S removal portion of the process.

The Stretford Process is then used to remove H_2S from the hydrogenated tail gas. This process involves absorption of the H_2S in an oxidizing alkaline solution. The oxidizing agents in the solution convert the H_2S to elemental sulfur, then are regenerated by air oxidation, which floats the sulfur off as a slurry. This sulfur slurry is then filtered, washed and melted to recover the Stretford solution and produce a high-purity sulfur product.

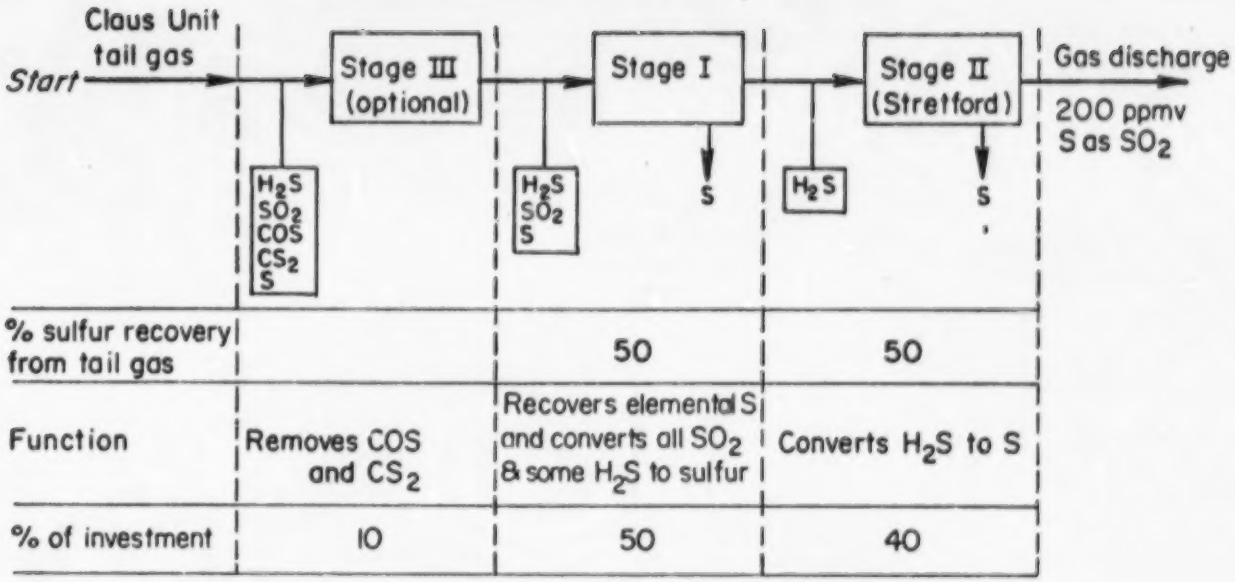
Operating conditions: The pressure drop for the treated gas is 2 to 3 psi; all pressures are near atmospheric. Operating temperatures are 550 to 750° F for the hydrogenation reactor and 70 to 120° F for the Stretford section. Equipment is essentially all carbon steel. The treated gas stream contains less than 100 ppm of total sulfur compounds and less than 10 ppm of H_2S. Spent oxidizer air is odorless, since it contains only air and water vapor.

Economics: Based on a plant treating the tail gas from a 100 lt/d sulfur plant. Investment: $700,000 to $1 million. Net utilities and chemical cost: $100 per day.

References: Beavon, D. K. and Vaell, R. P., "The Beavon Sulfur Removal Process for Purifying Claus Plant Tail Gas," 37th Mid-year Meeting, API Division of Refining, New York, May 9, 1972.

Commercial Installations: Eight Beavon Sulfur Removal plants are currently being designed and built in six locations in the United States and Japan.

Licensor: Union Oil Co. of California.



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Cleanair

Application: Recovers 99.9% of the sulfur from Claus plant tail gas, leaving no more than 200 ppmv SO_2 equivalent in the effluent.

Product: Sulfur produced is typically 99.5% pure elemental sulfur, but can be guaranteed to be 99.9% pure, based on total pit production. The sulfur is suitable for any ultimate use.

Description: The process is used to convert sulfur constituents in Claus plant tail gas to molten elemental sulfur. It is installed upstream of the incinerator in a conventional Claus plant, and may preclude the need for incineration. The process consists of three stages installed stepwise to achieve decreasing amounts of sulfur emitted to the atmosphere. Levels of not more than 200 ppmv SO_2 equivalent in the effluent can be guaranteed. The system may be installed on old Claus plants or on new Claus plants, but is somewhat more expensive on old Claus systems.

From a space standpoint, the process requires about the same amount of plot plan as a dual-train Claus plant. From an operating standpoint, the plant requires about 6 hours per 24 hours of operation. Other requirements per daily ton of sulfur produced in the Claus plant are: 8 pounds of steam per hour, 4 Kwh per hour, 9 gpm of water for cooling, and 10-25 cents per day for chemicals.

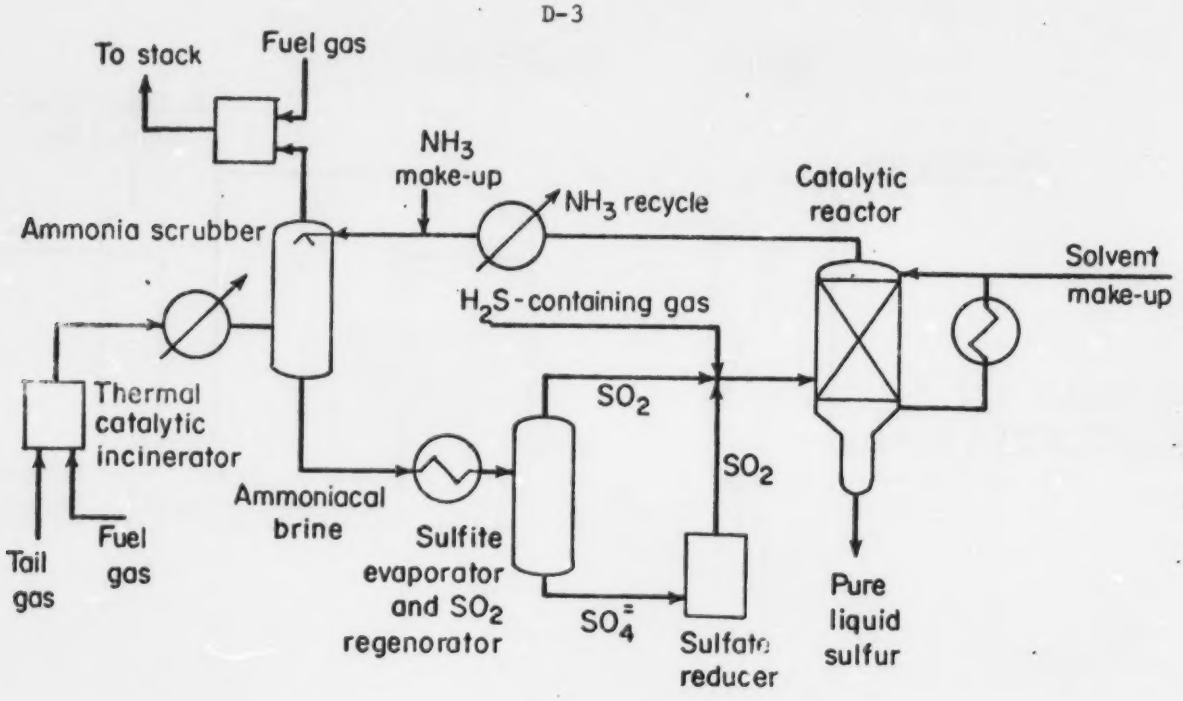
Stage one of the process removes the sulfur dioxide, stage two removes the hydrogen sulfide, and stage three removes the COS and the CS_2.

Economics: With a given amount of gas flow, which would result from a Claus plant being fed a constant amount of feed, the process plant cost is somewhat sensitive to the amount of sulfur being handled. Therefore, a unit for a Claus plant operating at a low efficiency is more expensive than one operating at a high efficiency. Taking, as an arbitrary number, a Claus plant operating at 95% efficiency, CLEANAIR process facilities can be provided for a 10-ton per day Claus plant for about $500,000. For a 1,000-ton-per-day Claus plant, this would be about $3 million.

Commercial installations: The first commercial installation was made at the Gulf Oil Corp. refinery at Philadelphia. This plant is guaranteed to provide a cleanup as low as 300 ppmv of sulfur dioxide equivalent. Several other CLEANAIR plants are in various stages of engineering and construction.

Reference: Proceedings of the 51st Annual Convention, Natural Gas Processors Association, April 10-12, 1972, New Orleans, La.

Licensor: J. F. Pritchard and Co.



IFP

Application: 1. Removal of H_2S and SO_2 from Claus unit tail gas to an SO_2 level of 1,500-2,000 ppm (IFP-1) or 500 ppm or below (IFP-2). 2. Stack gas clean-up to take SO_2 down to or below 500 ppm. (IFP-2).

Feed: Tail gas from 1, 2 or 3-reactor Claus plants or stack gas, as appropriate.

Product: Bright yellow sulfur, 99.9% pure, with 150 ppm max. ash and 150 ppm max. organic impurities.

Description. IFP-1 (not illustrated): Claus tail gas is injected into a packed tower and contacted contercurrent with solvent containing catalyst. Sulfur is formed, collected and removed from bottom of the tower. Operating temperatures in the tower range from 250 to 280 ° F. No booster blower on Claus tail gas is required due to low pressure drop design of tower. IFP-2 (illustrated): Claus tail gas after incineration is scrubbed with aqueous ammonia. Clean overhead is incinerated and vented up the stack. Brine containing sulfites, bisulfites and small amounts of sulfates from the scrubber is evaporated; sulfates are reduced, and mixed SO_2/NH_3 overheads are injected into the bottom of the contactor. An H_2S slipstream is also fed to the bottom of the contactor along with the SO_2 stream. Solvent containing catalyst is circulated countercurrent to the gas flow. Operating temperature in the contactor ranges from 250 to 280° F. Sulfur is formed, collected and removed from the bottom of the tower. Ammonia is removed overhead and returned to the scrubber.

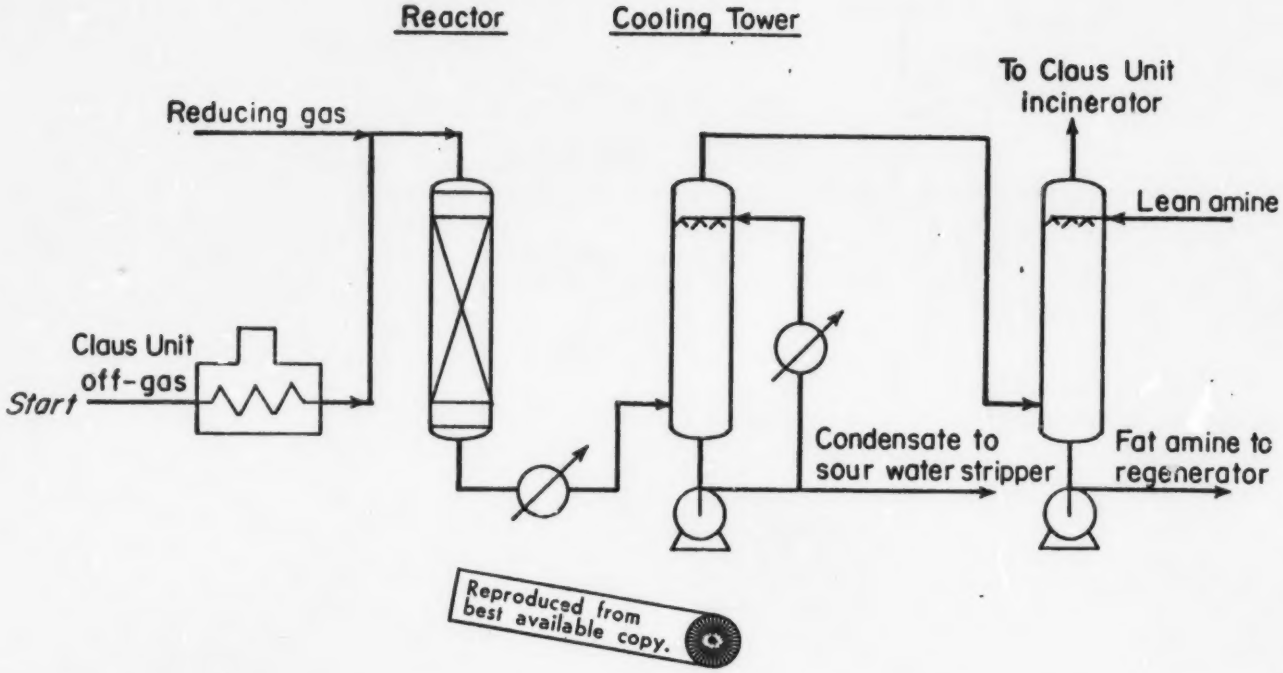
Operating conditions: The solvent temperature to the packed tower ranges from 250 to 280°F. The most important variable in the process is the ratio of H_2S/SO_2 in the feed to the packed tower. This ratio is held within a given range by appropriate analyzer-controller equipment.

Economics: An IFP-1 unit for an over-all recovery of 99% for use with a 1,400-T/d Claus plant that recovers 96.5% sulfur requires a battery limits investment of $2 million. Operating costs are: utilities—$30/d; catalyst and solvent—$347/d. Investment for a 200-T/d IFP-1 plant is of the order of $450,000. An IFP-2 plant added on to a 250-T/d Claus @ 95% recovery requires a battery limits investment of $800,000. Operating costs are: utilities—$70/d; catalyst and solvent—$5/d.

Commercial installations: IFP-1: Seven operating, five under construction for Claus plants with capacities from 5 to 2,400 T/d, totalling 4,000 T/d. IFP-2: One plant operating and one under construction.

Reference: Bonnifay, P. et al, "Partial and Total Sulfur Recovery," *Chemical Engineering Progress*, Vol. 68, No. 8, pp. 51-52, August 1972.

Licensor: Institut Français du Pétrole.



Reproduced from best available copy.

Shell Claus off-gas treating (SCOT)

Application: To increase the sulfur recovery efficiency of Claus units from the usual level of about 95% to more than 99.8%.

Description: The process essentially consists of a reduction section and an alkanolamine absorption section.

In the reduction section all sulfur compounds and free sulfur present in non-incinerated Claus off-gas are completely converted into H_2S over a cobalt/molybdenum catalyst at 300° C in the presence of H_2 or a mixture of H_2 and CO. Reducing gas can be supplied from an outside source, or a suitable reducing gas can be generated by substoichiometric combustion in the direct heater. This heater is required in any case for heating process gas to the reactor inlet temperature. Reactor effluent is cooled subsequently in a heat exchanger and a cooling tower. Water vapor in the process gas is condensed, and condensate is sent to a sour water stripper.

Cooled gas, normally containing up to 3% vol. H_2S and up to 20% vol. CO_2, is countercurrently washed with an alkanolamine solution in an absorption column specially designed to absorb almost all H_2S but relatively little CO_2. The treated gas from the absorption column, which contains only traces of H_2S, is burned in a standard Claus incinerator.

The concentrated H_2S is recovered from the rich absorbent solution in a conventional stripper and is recycled to the Claus unit.

Operating conditions: The process has a high flexibility to cope with variations in Claus plant operation; changes in the Claus off-gas composition have only a small effect on over-all sulfur recovery efficiency. Feed gas rates from 20 to 100% of design can be handled easily. No secondary waste streams are produced.

Units are designed for minimum pressure drop so that they can be added easily to existing Claus units.

Economics: Basis: Unit for a Claus unit 250 t/sd sulfur intake and a Claus unit sulfur recovery of 94%.

Utilities:

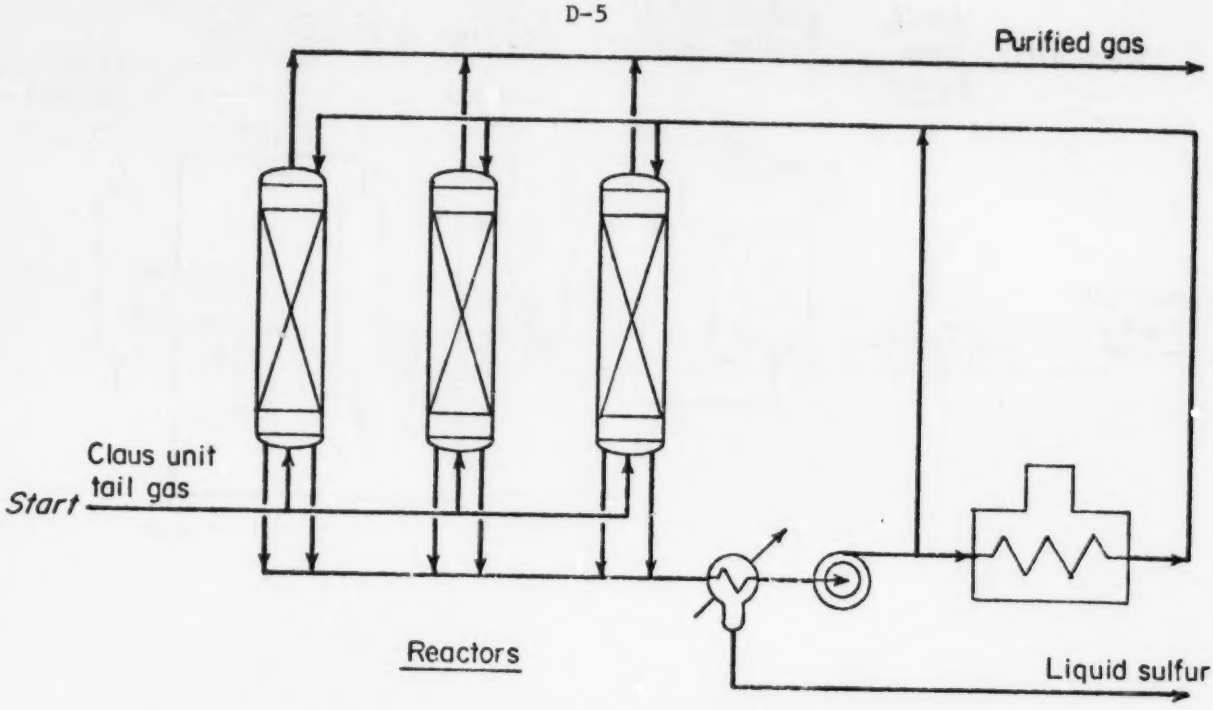
Boiler feed water	5,500 lb/h
LP steam (50 psig)	6,400 lb/h
Electricity	350 kW
Fuel gas (LHV 19,800 Btu/lb)	230 lb/h
Reducing gas (expressed in equivalent pure H_2)	53 lb/h
Operating data:	
Labor	1/6 operator/shift
Maintenance	2% on capital

Capital investment varies between 70 and 100% of the capital for the preceding Claus unit.

Commercial installations: Several units ranging in size from 10 to 2,100 t/sd equivalent Claus plant capacity are in various stages of planning, design and construction.

Reference: *Petroleum and Petrochemical International*, Vol. 12, No. 9, September 1972, pp. 54-58.

Licensing inquiries: Shell Development Co., Houston (USA), Nihon Shell Gijutsu K.K., Tokyo (Japan and Far East), Shell Internationale Research Mij. B.V., The Hague (rest of world).



Sulfreen

Application: Desulfurization of residue gas.

Charge: Claus unit tail gas.

Products: Liquid sulfur.

Description: The process is essentially an extension of the Claus process, except that H_2S and SO_2 are made to react at temperatures below the sulfur dew point of the reaction gas mixture:

$$2\,H_2S + SO_2 \longrightarrow 3\,S + 2\,H_2O + 35\ Kcal$$

Since equilibrium conversion becomes more complete as temperature is lowered, substantially higher sulfur recovery is possible than in a normal Claus plant. The reaction takes place in the presence of a catalyst, either alumina or special activated carbon.

Sulfur formed is adsorbed on the catalyst which eventually becomes saturated, requiring periodic regeneration by desorption of sulfur with hot gas.

The process reduces entrained sulfur to a minimum, as the catalyst acts as a very effective adsorbent for liquid sulfur. COS and CS_2 are not affected.

Unit operation is exceedingly simple and differs only slightly from that of a Claus unit. Since only solid adsorbents are used and no liquids except sulfur condense, the process is free of liquid waste disposal problems. Sulfur produced is bright yellow and of 99.9% purity.

A unit may consist of three reactors, two in adsorption and one in desorption service. The number of reactors is determined strictly by economic considerations. Desorption of sulfur is effected by means of hot gas in a closed cycle. Desorption gas, containing liquid sulfur is combined with Claus produced sulfur. Since produced sulfur is of the same quality no product contamination exists.

An alternate of the Sulfreen process involving two-stage treatment can provide over-all recoveries exceeding 99%. A two-stage Sulfreen unit consists of two catalytic beds in series. In the first bed H_2S and SO_2 form sulfur according to the Claus reaction; however, the ratio of H_2S/SO_2 is adjusted in such a manner that essentially all of the SO_2 is consumed and the effluent gas contains only H_2S. After addition of air to the first stage effluent, H_2S is oxidized directly to sulfur in the second stage.

With a 95% conversion in the Claus plant and COS and CS_2 content reducing the yield by 0.5%, an over-all yield around 99% (or higher with the alternate) can be obtained, with either catalyst.

Operating conditions: As all processes based on the Claus reaction, a control with an optimizer of the H_2S/SO_2 ratio is required in the reaction gas mixture at or near the stoichiometric proportion of 2:1 for optimum results. Pressure drop through the unit is in the order of 1.4-2 psi. Catalyst life expected: at least 4 years.

Investment/operating costs: Use of alumina catalyst permits carbon steel construction and gives a lower cost for the unit. Battery limits capital cost of a unit for a 1,000 ltpd sulfur plant will be around $2 million.

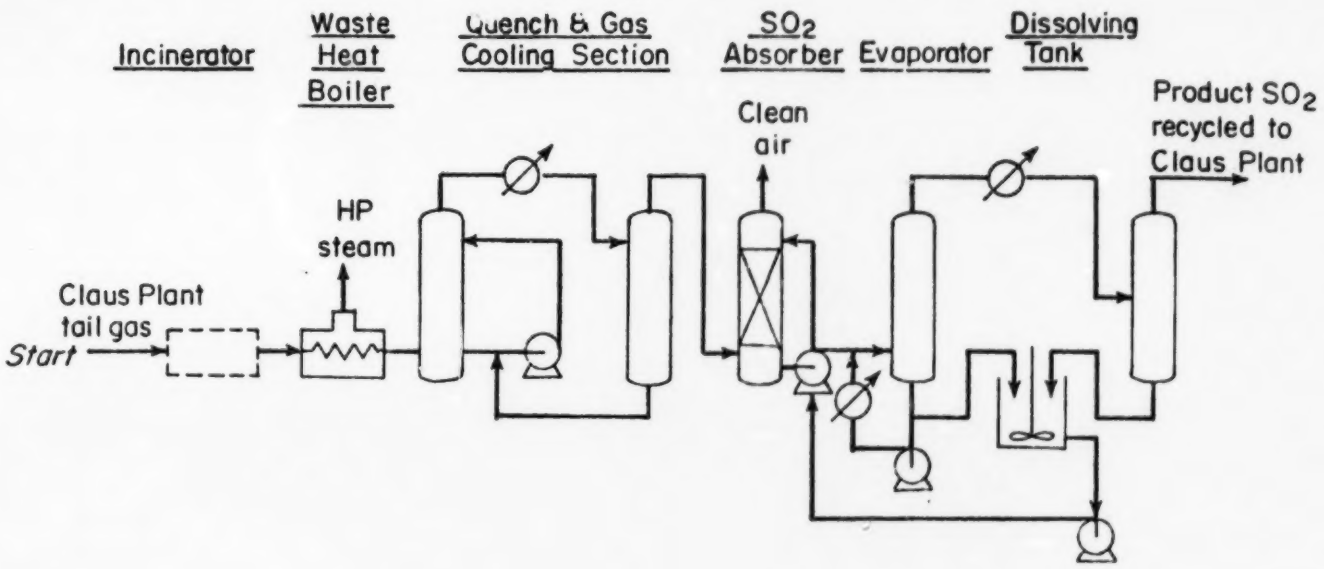
Utilities consumption will be as follows:

Electricity—650 Kwh
Boiler feed water—10 U.S. gpm
Fuel gas—0.35 MMscfd

Commercial installations: 2 onstream: One in France (1,000-t/d sulfur plant) and one in Canada (4,000-t/d sulfur plant). 3 in construction.

Reference: Guyot, G. and Martin, J. F., "The Sulfreen Process," Canadian NGPA, June 11, 1971.

Licenser: SNPA/Largi; The R. M. Parsons Co., engineering.



W-L SO_2 recovery

Application: Desulfurization of waste gas stream.

Feed: Tail gas from Claus units.

Products: Concentrated SO_2 gas suitable for recycle to Claus units or for further processing, e.g., to sulfuric acid.

Description: Tail gas from Claus sulfur units is first incinerated to convert all of the sulfur compounds originally present (H_2S, COS, CS_2, etc.) to SO_2. The hot gases are cooled in a waste heat boiler, then quenched and fed to the SO_2 absorber.

The absorber is fed a lean solution of sodium sulfite which absorbs the SO_2 by reacting with it to form sodium bisulfite. The clean gases pass to the stack, while the rich bisulfite solution is fed to an evaporator/crystallizer regeneration system. SO_2 and water vapor pass overhead from the evaporator to a condenser. A knockout drum separates condensed water for return to the absorbent dissolving tank and the product stream of concentrated, saturated SO_2 is piped back to the Claus plant feed or to other processing.

A stream of slurry is withdrawn from the evaporator and the sulfite crystals are redissolved to produce the lean solution for recycle to the absorber. The evaporator can be designed to use very low pressure exhaust steam (10-15 psig) as a heat supply.

A typical SO_2 recovery system for Claus units producing about 400 ltpd of sulfur is designed to treat 42,000 scfm of tail gas with initial SO_2 content in the range of 10,000 to 13,000 ppmv (1-1.3%, vol.). Effluents levels less than 100 ppmv SO_2 in the stack gas have been consistently achieved in commercial installations.

Yields: Sulfur oxide emissions in effluent stack gas can be reduced by as much as 99%. The product stream for recycle is 90-95% SO_2.

Economics: Investment for adding a SO_2 recovery system onto a typical existing 200-ltpd Claus unit is about $1.6 million (absorber and following).

Typical requirements:

Steam—High-pressure, produced	19,000 lb./hr.
Low-pressure consumed	14,000 lb./hr.
Net for export	5,000 lb./hr.
Connected H.P.	300
Cooling water	1,000 lb./hr.
Caustic make-up (100% NaOH basis)	1 tpd

Commercial installations: Five in operation; eight under construction or being engineered. Two of these treat Claus plant tail gas: one from three 150-ltpd units at Standard Oil of California's El Segundo, Calif., refinery, and another used for two 200-ltpd units at the Toa Nenryo Kogyo K.K. refinery in Kawasaki, Japan.

Licensor: Wellman-Power Gas, Inc.

APPENDIX E

DETAILS OF PLANT AND FIELD VISITS AND SAMPLE OF QUESTIONNAIRE SENT OUT FOR SOLICITING INFORMATION

Visits were made to the companies and the State Air Pollution Control Agency listed in Table E-1. The persons visited and a brief description of the nature of the visit are also presented in the table.

In addition to these visits, numerous (telephone) conversations were held with many industry experts in various areas. These experts are listed in Appendix F. Everyone of these experts were very helpful in providing without hesitation the information sought. Such information was quite useful in making this report accurate and current.

Details of the Questionnaire Sent Out

Copies of the questionnaire presented on pages E-3 and E-4 were mailed to the following: (1) Exxon Company USA (Production Department) Houston, Texas and (2) The Texas Mid Continent Oil Gas Association; the former provided helpful oral answers while the latter organization provided an excellent compilation of written answers to every question. This computation has been the source of much useful information base for this BCL report.

TABLE E-1. DETAILS OF PLANTS AND FIELD VISITS

Name of Plant/ Field Visited and Date of Visit	Persons Visited With and Nature of Visit	Name of Person(s) Visiting from BCL/EPA
Shell Oil Company Bryans Mill Processing Plant Bryans Mill, Texas March 9, 1974	Mr. Kenneth H. Rhoads Chief, Gas Plant Engineering Mr. John Flynn Process Engineer Discussed methods of H_2S recovery, etc., and visited Claus plant, and gas processing plant	Keshava S. Murthy, BCL
Texas Air Control Board Austin, Texas March 10, 1974	Mr. Charles R. Barden Executive Director Mr. Steve Spaw Director, Permits & Inventory Division Mr. Samuel Crowther Engineer Discussion of the extent of the SO_2 emissions and control problems related to oil and gas processing	Keshava S. Murthy, BCL
Exxon Company USA Production Department New Orleans, La. April 28, 1974	Mr. Charles Hagemeier Senior Technical Advisor Mr. Carl T. Hester Environmental Coordinator Discussion of Exxon's Jay Field facilities and reinjection as a means of control etc.	Charles B. Sedman, EPA Keshava S. Murthy, BCL
Exxon's Jay Field Gas Processing Facilities Pensacola, Florida April 29, 1974	Mr. John Barry Chambers Senior Engineer Plant visit and discussions	Charles B. Sedman, EPA Keshava S. Murthy, BCL

Information Requested by Battelle for the Preparation of a Document to Assist USEPA in Setting Performance Standards for Oil and Gas Producing and Processing Facilities

NOTE: The purpose of this information gathering is to get the opinion of the industry experts. The answers need not be typed or formal. These answers will not be held against anyone as legal. They will be kept as strictly confidential or destroyed if you so desire. Therefore, feel free to provide factual and critical opinions and support your opinion on solid data wherever possible.

Question 1: There are thousands of small gas producers/processors. The sour gas produced by small operations is usually treated in a conventional amine process. The spent amine solution is regenerated and the regenerator off-gases are flared. Some suggest that instead of the current practice of flaring, the off-gases (mainly H_2S and CO_2) can be reinjected to the well formations.

a. Do you agree that this is possible?

b. If yes, can you provide details of operations that are currently reinjecting?

c. If reinjection is not feasible, provide reasons why it is not feasible.

d. Define problems (corrosion, etc.) if reinjection is followed.

e. In summary, please provide sufficient factual information that would assist in forming definitive conclusions about the feasibility or otherwise of reinjection as a method of avoiding SO_2 pollution from flares in small plants.

Question 2: If reinjection discussed above is felt to be impractical as a method of disposal of flares, what other methods in your opinion are available as alternatives to flaring? Define briefly the economic and technical merits of the method suggested by you.

Question 3: What, in your opinion, should be the cut off point at which emission regulations for gas treating plants should be applicable (or not applicable). Justify you opinion with technical and economic data.

Question 4: The pipeline standard for H_2S is 1/4 grain/100 scf. Are you aware of any similar limitations on the concentrations of mercaptans (RSH), carbonyl sulfide (COS), and carbon disulfide (CS_2) by pipeline companies? If so, what are the standards and what is the basis for these established standards?

Question 5: Please provide the composition of your well head gas if available for H_2S, CO_2, COS, RSH, total sulfur, and hydrocarbons. (The well need not be identified by name or location if you wish to preserve secrecy.)

Question 6: List all problems (present and potential) that small and large gas processors will face if SO_2 emission regulations on processing plants are enacted at levels you consider to be uneconomic.

Question 7: Please provide a material balance flowsheet of the desulfurization plant for large natural gas plants you currently use. The flowsheet can be for any of the following: sulfinol, DEA, SNPA-DEA, MEA, Stretford ADA/Vandate, Giammarco-Vetricoke, DGA or Econamine or hot carbonate.

APPENDIX F

LIST OF INDUSTRY AND OTHER PERSONNEL
CONTACTED BY TELEPHONE AND VISITS

Mr. Elmer Berlie
Vice President
Western Research and Development Company
932, 700-6th Avenue
Southwest, Calgary, Alberta, Canada
(403) 263-1253

Mr. James C. Bouldin
Director
Rail Road Commission of Texas
Oil and Gas Division
Earnest O. Thompson Building
Teuth and Colorado Streets
Austin, Texas 78701

Miss Ailleen Cantrell
Director of Editorial Surveys
The Oil and Gas Journal
Petroleum Publishing Company
211 South Chayanne Street
Tulsa, Oklahoma 74101
(918) 584-4411

Mr. L. E. Cardwell
Helium Analysis Group
U. S. Bureau of Mines
Amarillo, Texas
(806) 376-2658

Mr. Samuel Crowther, P.E.*
Engineer
Permits & Inventory Division
Texas Air Control Board
8520 Shoal Creek Blvd.
Austin, Texas 78758

Mr. Jack C. Dingman
Jefferson Chemicals Company
Box 53300
Houston, Texas 77052
(713) 529-4471

Mr. Vincent R. Gurzo
Sales Engineer
Linde Molecular Sieve Products
Union Carbide Corporation
1300 Lakeside Avenue
Cleveland, Ohio 44114
(216) 621-4200

* Contact established by personal visit.

Mr. Charles E. Hagemeier*
Senior Technical Advisor
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Environmental Coordinator
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Mr. E. G. Hill
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National Tank Company
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Mr. Richard Jackson
Chief of Gas Engineering
Cities Service Oil Company
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Mr. Earl Jairus
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The Ralph M. Parson Company
617 West 7th Street
Los Angeles, California 90017
(213) 629-2484

Mr. Gordon Koelling
Natural Gas Division
U.S. Bureau of Mines
Arlington, Virginia
(703) 557-0239

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* Contact established by personal visit.

Mr. Larkin Kyle
Chief Engineer of Mechanical Design
Gas Engineering Office
Cities Service Gas Company
Oklahoma City, Oklahoma

Dr. R. N. Maddox
Head, School of Chemical Engineering
Oklahoma State University
Stillwater, Oklahoma
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Donald H. McCrea
Manager, Process Development
Benfield Corporation
615 Washington Road
Pittsburg, Pa. 15228
(412) 344-8550

Mr. Jack McWilliams
Division Environmental Coordinator
Ampco Production Company
Houston Division
500 Jefferson Building
P. O. Box 3092
Houston, Texas 77001
(713) 227-4371

Mr. Kenneth H. Rhoads (John Flynn)*
Chief, Gas Plant Engineering
Exploration and Production
Shell Oil Company
Two Shell Plaza
P. O. Box 2099
Houston, Texas 77001
(713) 220-5446

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* Contact established by personal visit.

APPENDIX G

CONVERSION FACTORS

To convert from Metric to English units, use reciprocal of given factors.

To Convert (English)	To (Metric)	Multiply by
actual cubic ft/min (acfm)	cu.m/hr	1.70
atmospheres (atm)	kilogram/Cm^2	1.033
barrels of oil (bbl)	kiloliters (kltr)	0.159
barrels of oil (bbl)	U.S. gallons	42
cubic feet (cft)	cubic meters (cum)	0.02832
cubic feet (cft)	litres (l)	28.32
cubic meters (cum)	cubic feet (cft)	35.31
°F	°C	subtract 32 then multiply 0.5556
ft	meter (m)	0.305
ft/sec	m/sec	0.305
gal/Mcf	l/cum	0.134
gpm	l/min	3.79
gpm/ft^2	l/min/m^2	40.8
grains (gr)	milligrams (mg)	64.8
grains (gr)	pounds (lb)	0.00014
gr/scf	gm/m^3	2.29
grains/100 scf	mg/s cu m	22.9
in.	cm	2.54
in. H_2O	mm Hg	1.87
lb-moles	gm-moles	454
lb-moles/hr	gm-moles/min	7.56
lb-moles/min	gm-moles/sec	7.56
long ton (LT - 2240 lb)	metric ton (MT)	1.0084
pounds (lb)	grains (gr)	7000
pounds/sq. in. (PSI)	atmospheres (atm.)	0.068
pounds/sq. in. (PSI)	kilogram/Cm^2 (kg/cm^2)	0.0703
ton (2000 lb)/month	metric ton/day (MT/D)	0.02926
tons	kilograms (kg)	907.2

APPENDIX H

HANDLING OF WASTE GAS WITH HIGH H_2S CONTENT

(Courtesy of Mr. Jack McWilliams,
Mid-Continent Oil & Gas Association, Dallas, Texas)

The corrosivity of waste gases containing hydrogen sulfide can vary considerably due to the gas composition, temperature, pressure, moisture or water content, velocities, etc. The selection of the proper metallurgy, need for protective coatings or use of inhibitors or neutralizers can best be made when the above conditions can be accurately defined.

Some general guidelines for handling these waste gases are listed below.

(1) You will not have corrosion if moisture is not present. However, it is not safe to assume that because dehydration facilities are installed that the gas will be kept dry at the operating conditions. Dehydrators are notorious for having malfunctions resulting in some moisture or water to get into the line. It quite often takes a considerable amount of time before this moisture is reabsorbed into dry gas.

(2) Hydrogen sulfide can form a liquid at moderate temperatures and pressures. At approximately 1000 psi and ambient temperature, some mixtures of H_2S and natural gas will contain liquid rich in H_2S.

(3) In field operations even when very high concentrations of H_2S are present, corrosion rates are relatively low. The reason for this is not known; however, it is partly due to (1) the poisonous and corrosive nature of H_2S results in a high degree of awareness and effort on the part of all personnel to assure that corrosion mitigation and monitoring programs are rigidly followed; (2) sulfur or iron sulfide may form a very tough protective scale on the steel which minimizes corrosion.

(4) It is important that velocities be kept as low as possible since high velocities (particularly when any liquids or abrasive materials such as sand or scale particles are present) tend to remove any protective film or scale buildup and cause corrosion reactions to proceed at a high rate.

(5) The formation of iron sulfide can cause plugging of the formation you are injecting into as well as causing corrosion. It should also be noted that iron sulfide upon exposure to air rapidly oxidizes to iron oxide.

(6) Hydrogen sulfide or other corrosion can cause hydrogen blistering or embrittlement (stress cracking) to take place depending on temperatures and pressures. To prevent this, metals below Rockwell "C" hardness of 22 are used in this type service. In wells handling streams containing H_2S, C-75 or softer tubing or casing are usually used. It must be remembered that prior to the last few years, API Grades J, K, and N pipe had only a minimum yield but no maximum value. Therefore manufacturers could substitute API Grade N or P grade pipe for J or K grade if the company so desired. This could be disastrous if the higher strength steel is used in the well containing high H_2S and a catalyst such as mentioned in Item 7 is used. Instant failures in tubing couplings, sucker rods have occurred under these conditions.

(7) Any low pH material such as dissolved CO_2, hydrochloric and other acids, or arsenic compounds (rarely used acidizing inhibitors) can act as a catalyst for stress corrosion and can cause rapid failure of highly stressed, high-strength steel. For example, acidizing a well equipped with N-80 or P-105 tubing (Rc above 22) that has been exposed to high H_2S concentrations can result in immediate tubular goods failures probably in the highly stressed couplings.

(8) For steel tubing and line pipe it is generally necessary to use corrosion inhibitors, plastic coatings, or cement linings as applicable to prevent corrosion. Most plastic coatings are not effective in very high H_2S and CO_2 environments or high temperatures and should be only used

after extensive testing or investigation based on similar operating conditions. Cement linings are effective except that if the pH is below 5 to 5.5 the cement will be dissolved by the acids formed. Oil or scale tends to form a protective coating on the cement and increase its acid tolerance to some degree.

(9) Copper and many copper alloys tend to corrode at extremely high rates in the presence of H_2S.

(10) High strength stainless steel tends to embrittle in high H_2S concentrations. Certain heat treated stainless steels with a low hardness are satisfactory. Monel and Inconel (although expensive) is an excellent material in a severely corrosive H_2S service.

(11) When designing any system, the conditions should be compared with similar systems in operation. Also any potentially corrosive system installed should have corrosion monitors at key points. These monitors such as corrosion coupons, electronic devices, etc. allow the corrosivity of the system to be measured. This will allow any changes to be made in corrosion mitigation programs prior to extensive damage occurring.

(12) Attached is a reference that will be helpful in designing a system.

(13) All welds in piping used in high hydrogen sulfide system should be normalized (heat treated) or stress relieved prior to use to prevent sulfide stress cracking and galvanic corrosion between the weld metal and the steel. In mildly corrosive environments the use of pre-heat and post-heat welding techniques are generally effective. This spreads out the heat affected zone and minimizes galvanic action. This is discussed in the attached material.

APPENDIX I

LIST OF CLAUS PLANTS IN NATURAL GAS PROCESSING

APPENDIX I. LIST OF CLAUS PLANTS IN NATURAL GAS PROCESSING

State/Company/City, County	Year Sulfur Production Started	Sulfur Production in 1973 (MT/D)	Sulfur Design Capacity (MT/D)
ALABAMA			
Humble Oil & Refining Co.			
Flomaton, Escambia	1972	(-)	136
Stauffer Chemical Co.			
LeMoyne	Before 1962		127
Expansion	Before 1972		+123
ARKANSAS			
Arkla Chemical Corp.			
Magnolia, Columbia	Before 1962		19
Expansion	1962	5.3	+11
Olin Corporation			
McKamie, Lafayette	1944		100
CALIFORNIA			
Lomita Gasoline Company			
Long Beach, Los Angeles	1971		Not reported
FLORIDA			
Amerada Hess Corporation			
Jay, Santa Rosa	1972		120
Humble Oil & Refining Company			
Jay, Santa Rosa	1971		14
Expansion	1972		+360
Louisiana Land & Exploration Co.			
Jay, Santa Rosa	1972		82
Louisiana Land & Exploration Co.			
Escambia County	1972	650**	88
MISSISSIPPI			
Elcor Chemical Corporation			
Canton, Madison	1965		12 Standby
Shell Oil Company (3-Stage Plant 97%)			
Jackson*	1972	500	1250
Shell Oil Company (2-Stage Plant Being Upgraded)			
Goodwater, Clarke	1971	1.4	35

(-) Blank spaces signify data not available

APPENDIX I. (Continued)

State/Company/City, County	Year Sulfur Production Started	Sulfur Production in 1973 (MT/D)	Sulfur Design Capacity (MT/D)	
NEW MEXICO				
Amoco Production Company				
Artesia, Eddy	1960	24.3	26	
Cities Service Oil Company				
Milnesand, Roosevelt	1967	8.0	20	
Climax Chemical Company				
Oil Center, Lea	1962		18	
Marathon Oil Company				
Indian Basin, Eddy	1967		36	
Northern Gas Products Co.				
Hobbs, Lea	1969		13	
Warren Petroleum Corporation				
Tatum, Lea	1961		4	
NORTH DAKOTA				
Texaco, Inc.				
Lignite, Burke	1961		20	
OKLAHOMA				
Pioneer Natural Gas Co.				
Madill, Marshall	1967		8	
J. L. Parker Company				
Madill, Marshall	Before 1961		15	Standby
TEXAS				
Amarillo Oil Company				
Waha, Pecos	1971		2	
Marathon Oil Company				
Raan, Pecos	1967		13	
Mobil Oil Corp.				
Coyanosa, Pecos	1967		29	
Texas American Sulfur Co.				
Sand Hills, Crane	1966		15	
Phillips Petroleum Company				
Crane County	Before 1961		100	
Expansion	1962		+65	
Warren Petroleum Corp.				
Waddell, Crane	Before 1961		50	
Expansion	1968	89.0	+45	

APPENDIX I. (Continued)

State/Company/City, County	Year Sulfur Production Started	Sulfur Production in 1973 (MT/D)	Sulfur Design Capacity (MT/D)
Warren Petroleum Corp.			
San Hills, Crane	1964	34	50
Northwest Production Corp.			
Big Lake, Reagan	Before 1962		3
Expansion	1962		+5
Sid Richardson Carbon & Gasoline Co.			
Kermit, Winkler	Before 1961		5
Wanda Petroleum Company			
Kermit, Winkler	1967		18
Amarillo Oil Col.			
Goldsmith, Ector	1967		5
Amoco Production Co.			
North Cowden, Ector	1952	26	26
Odessa Natural Gasoline Co.			
Odessa, Ector	1961	12.8	13
J. L. Parker Company			
Penwell, Ector	Before 1962		30
Phillips Petroleum Co.			
Goldsmith, Ector	Before 1961		75
Elcor Chemical Corp.			
Midland, Midland	1958		1 Standby
Amoco Production Co.			
Midland Farms, Andrews	1956	6	11
Amoco Production Co.			
South Fullerton, Andrews	1968	3	6
J. L. Parker Co.			
Andrews, Andrews	Before 1961		15
Amoco Production Co.			
Sundown, Hockley	1951	34	48
Cities Service Oil Co.			
Welch, Dawson	1970	2	4
Cities Service Oil Co.			
Seminole, Gaines	Before 1961	23	28
Cities Service Oil Co.			
Lehman, Cochran	Before 1972	2	4
Cities Service Oil Co.			
Lehman, Cochran	1962		9
Diamond Shamrock Corp.			
Sunray, Moore	1951		30

APPENDIX I. (Continued)

State/Company/City, County	Year Sulfur Production Started	Sulfur Production in 1973 (MT/D)	Sulfur Design Capacity (MT/D)	
Texas Sulfur Products Inc.				
Dumus, Moore	1966		13	
Trans-Jeff Chemical Corp.				
Tilden, McMullen	Before 1962		20	
Expansion	1962		+80	
Atlantic Richfield Co.				
Fashing, Atascosa	Before 1961		10	
Elcor Chemical Corp.				
Fashing, Atascosa	1960		55	
Humble Oil & Refining Co.				
Jourdanton, Atascosa	1967	13.2	22	
Warren Petroleum Corp.				
Fashing, Atascosa	Before 1962	27.4	45	
Shell Oil Co. (2-Stage Plants Feed to a Common 3rd Stage)				
Person, Karnes	1962		12	
Expansion	1965		+23	
Coastal States Gas Producing Co.				
Kenedy, Karnes	1968		9	
Olin Corp.				
Beaumont, Jefferson	1959		50	Standby
Amoco Production Co.				
Edgewood, Van Zandt	1964	332	576	
Cities Service Oil Co.				
Myrtle Springs, Van Zandt	1968	216	270	
Amoco Production Co.				
West Yantis, Wood	1963	34	80	
Getty Oil Co.				
Cayuga, Anderson	Before 1972		130	
Getty Oil Co.				
Winnsboro, Franklin	1969		224	
Shell Oil Company (3-Stage, 97%)				
Bryan's Mill, Cass	1962	190	200	
Texaco, Inc.				
Dunbar, Rains	1966		70	
Warren Petroleum Corp.				
Sulphur Springs, Hopkins	1965	40	89	

APPENDIX I. (Continued)

State/Company/City, County	Year Sulfur Production Started	Sulfur Production in 1973 (MT/D)	Sulfur Design Capacity (MT/D)	
UTAH				
Union Oil Co. of California				
Lisbon, San Juan	1967		10	
WYOMING				
Amoco Production Co.				
Riverton, Fremont	1965	39	70	
Atlantic Richfield Co.				
Riverton, Fremont	1963		12	
Western Nuclear, Inc.				
Riverton, Fremont	1968		5	
Amoco Production Co.				
Powell, Park	1949	32	110	
Chem-Gas Products Co.				
Powell, Park	1961		14	
Husky Oil Co.				
Ralston, Park	1964	29	32	
Expansion	1966		+15	
Amoco Production Co.				
Worland, Washakie	1958		22	Standby
Texas Gulf Sulfur Co.				
Worland, Washakie	1950		400	Standby
Jefferson Lake Sulfur Co.				
Manderson, Big Horn	Before 1959		113	Standby
Atlantic Richfield Co.				
Sinclair, Carbon	Before 1962		26	
Signal Oil & Gas Co.				
Nieber Dome	Before 1962		50	
Texas-Seaboard Inc.				
Silvertip	1957		50	Standby
TOTAL	84 Plants	(Incomplete)	6249	

* Field deliverability limited production of sulfur

** These fields are unitized and the total sulfur production in 1972 was 650 MTD

Blank spaces indicate data not available